REPORT ON LAWRENCE BERKELEY LABORATORY

Exploratory Research and Development Fund

FY 1991

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Lawrence Berkeley Laboratory

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Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

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Introduction

The *Lawrence Berkeley Laboratory Exploratory R&D Fund FY 1991* report is compiled from annual reports submitted by principal investigators following the close of the fiscal year. This report describes the projects supported and summarizes their accomplishments. It constitutes a part of an Exploratory R&D Fund (ERF) planning and documentation process that includes an annual planning cycle, projection selection, implementation, and review.

The LBL ERF program is a critical tool for directing the Laboratory's forefront scientific research capabilities toward vital, excellent, and emerging scientific challenges. The program provides the resources for LBL scientists to make rapid and significant contributions to critical national science and technology problems. The ERF also advances the Laboratory's core scientific capability and permits exploration of exciting new opportunities. Areas eligible for support include:

- Work in forefront areas of science and technology that enrich Laboratory research and development capability;
- Advanced study of new hypotheses, new experiments, and innovative approaches to develop new concepts or knowledge;
- Experiments directed toward proof of principle for initial hypothesis testing or verification; and
- Conception and preliminary technical analysis to explore possible instrumentation, experimental facilities, or new devices.

The ERF program supports LBL's mission in many ways. First, because ERF funds can be allocated in a relatively short time frame, LBL researchers can support the mission of DOE and serve the needs of the nation by quickly responding to forefront scientific problems. Second, ERF enables the Laboratory to attract and retain highly qualified scientists, and supports their efforts to carry out world-leading research. Finally, the ERF program also supports new projects that involve graduate students and postdoctoral fellows, thus contributing to the education mission of the Laboratory.

LBL has a formal process for allocation of funds for ERF. The process relies on individual scientific investigators and the scientific leadership of the Laboratory to identify opportunities that will contribute to scientific and institutional goals. The process is also designed to maintain compliance with DOE Orders. From year to year, the distribution of funds among the three scientific program areas will change. This flexibility optimizes the Laboratory's ability to respond to opportunities.

Laboratory ERF policy and program decisions are the responsibility of the Laboratory Director. The Director has assigned general programmatic oversight responsibility to the Laboratory Deputy Director. Administration and reporting on the ERF program is supported by the Office for Planning and Development. ERF accounting procedures and financial management are consistent with the Laboratory's accounting principles and stipulations under the contract between the University of California and the Department of Energy, with accounting maintained through the Laboratory's Chief Financial Officer.

In FY 1991, LBL was authorized by the Department of Energy to establish a funding ceiling for ERF of 3% of the Laboratory's FY 1991 operating budget. This funding level was provided to develop new scientific ideas and opportunities and allow the Laboratory Director an opportunity to initiate new directions. However, budget constraints limited available resources, so only $3.2 M was allocated.

In FY 1991, scientists submitted more than 110 proposals requesting almost $10 M. A total of 26 projects were funded in FY 1991, with awards ranging from $43 K to $348 K. These projects are summarized in Table 1.

Table 1. FY 1991 Exploratory R&D Fund.

Division	Investigator	Project Title	($)
Accelerator and Fusion Research Division			
	D.J. Attwood A. Neureuther W.G. Oldham J.B. Kortright J.H. Underwood	Reduction X-Ray Lithography	97,900
	S. Chattopadhyay R. Gough K.-J. Kim	Investigation of IR and UV FELs at LBL	348,100
Applied Science Division			
	S. Cramer	High Resolution Soft X-Ray Absorption Spectroscopy of DNA and Derivatives	176,500
	J.M. Daisey M.T. Smith R.C. Spear	Biologically-Based Risk Assessment: A Novel Approach Based on First Principles	85,000
Cell and Molecular Biology Division			
	J. Campisi	Protooncogenes and Tumor Suppressor Genes in Normal and Transformed Growth Control	147,200
	P. Yaswen	Calcium Signal Transduction during Human Mammary Carcinogenesis	75,000
Chemical Biodynamics Division			
	A.N. Glazer R.A. Mathies	Novel Fluorescent Probes from Nucleic Acid-Dye Complexes	54,100
Chemical Sciences Division			
	D.A. Shirley	Molecular Beam Threshold Time-of-Flight Spectroscopy of Rare Gas Atoms	43,200
	Y.T. Lee A.H. Kung	Technical Evaluation of Beamlines and Experimental Stations for Chemical Dynamics Applications at the ALS	110,500
Earth Sciences Division			
	T.V. McEvilly W.F. Kolbe E. Katz M.J. Pollard	Displacement Detectors for Seismometry	59,300
	P.L. Williams	Advancement of Fault Assessment Techniques and Improving Estimates of Seismic Risk at LBL	69,100

Table 1. Continued.

Division	Investigator	Project Title	($)
Materials Sciences Division			
	P. Alivisatos	Semiconductor Thin Films Using Nanocrystals Precursors	71,200
	D.S. Chemla	Quantum size Effect in Semiconductor Nanostructures	346,100
	M.L. Cohen A. Zettl	Superior Superconducting Materials	100,600
	C.S. Fadley	Surface, Interface, and Nanostructure Studies Using Synchrotron Radiation in Combination with Other Probes	193,900
	R. Gronsky	Technical Assessment of New Methodologies for 1 Å Imaging Resolution in a Transmission Electron Microscope System	92,700
	J. Orenstein	Terahertz Electrodynamics of Materials	90,100
	G.M. Rosenblatt	Human Studies of Materials and High Temperature Systems	213,900
	C.V. Shank	Femtosecond Dynamics in Condensed Matter	268,200
	J.A. Yarmoff	Stimulated Desorption of Halogens	42,200
Nuclear Science Division			
	C.R. Gruhn	Prototype Tracking and Timing Detectors for RHIC	102,300
Physics Division			
	M. Gilchriese	Silicon Tracking System R&D	101,200
	M. Levi	Data Acquisition Electronics R&D	107,000
Research Medicine and Radiation Biophysics Division			
	T.F. Budinger D.T. Attwood	ALS Life Sciences Initiative	75,000
	T.L. Hayes	Viability in Synchrotron Microscopy	32,000
	W.W. Moses S.E. Derenzo	Scintillation Mechanisms of Heavy Atom Scintillators	49,700
TOTAL			3,152,000

Project Reports

Accelerator and Fusion Research Division

Reduction X-Ray Lithography

Principal Investigators: David J. Attwood, Andrew Neureuther, William G. Oldham, Jeffrey B. Kortright, and James H. Underwood

Funding: $97,900

Project Description

It has become a national need to develop novel, effective approaches to produce "nanochips," with feature sizes deep into the submicron range, using x-ray lithography. With the Center for X-Ray Optics, the Advanced Light Source, a strong collaboration with the Electrical Engineering and Computer Science Department at UC-Berkeley, and interest from industrial partners, LBL found itself in a unique position to participate in this research effort. The long-term goal of the program is to establish LBL as a research base for advanced (5- to 10-year outlook) x-ray-lithography R&D.

In 1990 and 1991, the program focused on identifying and defining technical requirements of new facilities for reduction x-ray lithography and for developing relationships within the advanced-semiconductor and x-ray lithography communities and then, building on that foundation, identifying appropriate experimental facilities and R&D programs.

Accomplishments

A formative workshop was held in January 1991 to help researchers in government and industry work together toward a strategy for developing an advanced manufacturing capability in the U.S. It familiarized researchers from the semiconductor lithography industry with the capabilities of the ALS and user access to it, and also helped us to understand industry's needs. Technical discussions resulted in consensus on three key issues:

- The x-ray lithography community would benefit from synchrotron radiation beams from both a bending magnet and a high-brightness undulator. This combination could supply a registration and metrology station and an easily accessible facility for basic testing of components, resists, and masks. There would also be sophisticated testing capabilities for optical elements, optical systems, and various projection technologies that have yet to be developed.
- The time frame for research activities at the ALS (that is, beginning in 1993) is well-matched to industry's needs for pattern transfer below 0.15 μm in the year 2000 and beyond.
- Development of production technologies for structures of these dimensions will require a nearby supporting infrastructure for nanostructure pattern generation, masks, optical coatings, resists, and the requisite synthesis and processing operations.

An advisory group including industry, university, and national-laboratory representatives met six times in 1991 to develop the specific focus of the program. Their efforts culminated in a conceptual plan that identifies the necessary specialized facilities and infrastructure for a reduction x-ray lithography program. These efforts recently resulted in a strong interest to support the development of new specialized facilities from the Defense Advanced Research Projects Agency.

Investigation of IR and UV FELs at LBL

Principal Investigators: Swapan Chattopadhyay, Richard Gough, and Kwang-Je Kim

Funding: $348,100 (FY 91)
$332,200 (FY 90)

Project Description

This project is continuing the investigation of the physics and technology of accelerators and optical systems for ultraviolet (UV) and infrared (IR) free-

electron lasers (FELs), with the eventual goal of identifying unique, next generation research facilities.

The research was mainly applied to UVFEL studies, where there are still many questions in the basic physics of short-wavelength FELs and in methods of generating suitable electron beams. The main tools were theoretical analysis, computation, and conceptual exploration of various parameter regimes. The developmental mode applied more to the IRFEL, where there was a clear understanding of the physics and operational requirements, but where there was a need to develop and assess technologies for robust and stable operation of an IRFEL for scientific experimental use. There was a critical evaluation of the state-of-the-art technologies and modifications.

Accomplishments

Assessment and design of an UVFEL facility rely upon quantitative understanding of the laser growth rate and saturated power, taking into account various realistic inhomogenous and perturbative effects. This understanding is being used to estimate design parameters. Despite the vast literature on the subject, such understanding is still evolving. In the previous fiscal year (1990), with ERF support, a clear analytical and quantitative understanding of the FEL gain mechanism was established, which allowed estimating realistic laser growth rates while taking into account various incoherent effects. In 1991, an equally deep understanding focused on the resulting saturated laser power, taking into account various inhomogenous effects such as the energy spread and emittance of the electron beam. This understanding has evolved to a point where one can readily examine, with confidence, various schemes of increasing the saturated power, such as prebunching, tapering, etc.

Extensive studies of storage-ring-based UVFELs had been performed in the group in previous years. The focus of research in 1991 was on linac-based UVFELs. A quantitative analytical understanding of the intrinsic differences between linacs and storage rings as drivers of FELs, from the FEL and accelerator-physics point of view, has been achieved. In addition, characteristics and design of high-brightness electron sources for linac-based FELs have been established.

Finally, several necessary follow-on research directions from these studies were identified:

- Physics and technology of ultrashort x-ray pulse generation.
- Experimental investigation of superconducting rf cavities via studies of microphonics.
- Laser-cavity interactions and short-pulse diagnostics.

Publications

Journals and Proceedings

S. Chattopadhyay, "On Storage Rings for Short Wavelength FELs," in *Proceedings of SPIE*, LBL-28483 (1990).

K.J. Kim, "Note on rf Photocathode Gun," BNL-52273 (1990); in *Proceedings* of the Workshop on 1A FELs (1990), p. 121.

K.J. Kim, "Spectral Bandwidth in Free Electron Laser Oscillators," *Phys. Rev. Lett.*, in press (1991).

Other Publications

K.J. Kim, "FEL Gain Taking into Account Diffraction and Electron Beam Emittance: Generalized Madey's Theorem," LBL-30628 (1991).

Y.H. Chin, K.J. Kim and M. Xie, "Three-Dimensional Free Electron Laser Dispersion Relation Including Betatron Oscillations," LBL-30673 (1991).

S. Chattopadhyay and K.J. Kim, "On Generation of Ultrashort X-Ray Pulses," in preparation (1991).

Applied Science Division

High Resolution Soft X-Ray Absorption Spectroscopy of DNA and Derivatives

Principal Investigator: Stephen Cramer

Funding: $176,500

Project Description

This project develops a fundamental understanding of the K-edge spectra of nitrogen in DNA and related small molecules. Project goals include refinement of experimental procedures for soft x-ray spectroscopy, observation of spectral changes due to metal complexation or halogenation of DNA, and investigation of soft x-ray photochemistry.

Accomplishments

Nitrogen K-edge spectra have been recorded for the normal DNA bases and nucleotides, as well as nucleotide polymers and natural DNA. The $1s \rightarrow \pi^*$ region changes upon forming the nucleotide base-sugar C-N linkage. The DNA spectrum can be simulated as the sum of constituent nucleotide spectra, and it is clearly different from the spectrum of a typical protein.

This information may be useful for DNA or protein-specific imaging in an x-ray microscope. A microscope tuned to 401 eV would be particularly sensitive to aromatic nitrogen such as DNA, while a 403 eV image would enhance relative sensitivity to protein amide nitrogen. From the fine structure of the $1s \rightarrow \pi^*$ region, local GC/AT ratios could also be determined. A full paper describing this work has been submitted to Biochemistry.

Biologically-Based Risk Assessment: A Novel Approach Based on First Principles

Principal Investigators: Joan M. Daisey, Martyn T. Smith, and Robert C. Spear

Funding: $85,000 (FY 91)
$50,000 (FY 90)

Project Description

Current methods for determining risks from low level but continuous exposures to toxic chemicals found in indoor air are scientifically flawed and may overestimate risk by orders of magnitude. Human health risk assessment would be much improved if biologically-based models could be used to extrapolate data from laboratory experiments to predict risk. In FY 1990, an interdisciplinary and UC inter-institutional research project was initiated to begin to change environmental health risk assessment by placing it on a more fundamental scientific basis in order to address the national problem of risk assessment for humans exposed to environmental pollutants.

The specific goals of the research were:

1. To complete the feasibility study (initiated in FY 1990) of the use of biologically-based risk modeling as a new approach to risk assessment, and
2. To establish an interdisciplinary and inter-institutional research project in this area.

The approach for the development of the biologically-based risk model was to link a

physiologically-based pharmacokinetic (PBPK) model for benzene with one or more cancer models and to evaluate their use with indoor air exposure data for occupational and general population exposures. The PBPK benzene model, developed by Bois et al., uses ranges of input parameters, which are statistically sampled, rather than a single, fixed value of each. This approach reflects the intrinsic variability of the population and provides outputs that are distributions of risks, as shown in the work done in FY 1990. Efforts to develop and apply a new mutation assay, HLA-A, to generate input data for the cancer model, were also undertaken.

Accomplishments:

Model Development and Application. In FY 1991, the PBPK model for rats was modified to include metabolites of benzene and modified for use for humans. The model was then used to explore the effect of exposure rate on tissue levels of various metabolites of benzene. Significant differences would implicate exposure intensity as well as total exposure as a causal factor in the adverse health effects of benzene and would support the need for a short-term exposure standard.
Metabolite formation was compared following exposure to benzene over the course of an 8-hour work day and following a single peak exposure for 15 minutes (Figure 1). These 8 ppm-hour total exposures were based on the permissible exposure limit (PEL) and short-term exposure limit (STEL) for benzene, set by the Occupational Safety and Health Administration. The model was parameterized using *in vitro* and *in vivo* experimental data on benzene toxicokinetics and metabolism.

The results of the modeling showed no differences between the two exposure conditions for tissue levels of the primary metabolites, benzene oxide and phenol. However, the model indicated that the amounts of the secondary metabolites, hydroquinone, catechol and muconaldehyde, formed in the body following a peak exposure of 32 ppm of benzene over 15 minutes are, on average, 20% higher than those formed following an equivalent exposure of 1 ppm over an 8 hour period. These metabolites are the crucial components of benzene toxicity to the bone marrow. Thus, a peak exposure may result in disproportionate damage relative to an equivalent exposure over an 8 hour period. These results, although not conclusive, provide the first scientific evidence in support of the need for a STEL for benzene. Efforts are now underway to examine dose-rate effects at levels of exposures commonly experienced by the general population.

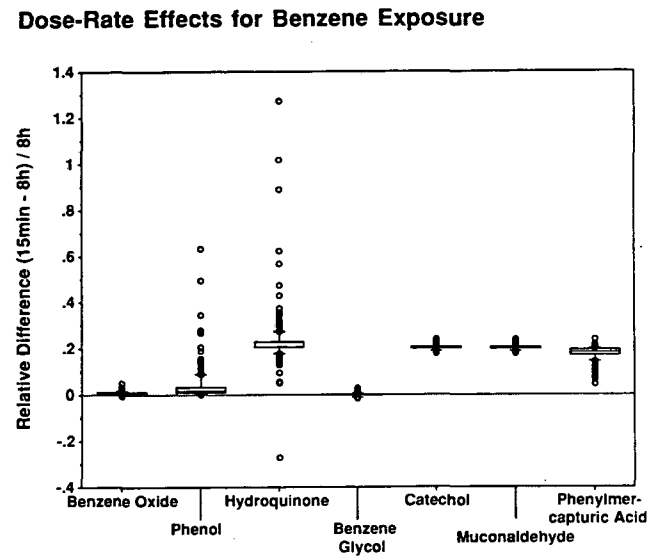

Fig. 1. Differences in total amount of benzene metabolites formed in the body per day, after exposures at 1 ppm for 8 hr compared to peak exposure at 32 ppm for 15 min, based on PBPK model simulations. Concentrations of hydroquinone, catechol, muconaldehyde and phenylmercapturic acid were increased by 20% on average for the peak exposure. The first three of these compounds are suspected to be directly involved in the carcinogenicity of benzene.

HLA-A Human Mutation Assay. In parallel with the modeling work, research was initiated on the development of a new human mutation assay. The HLA-A assay is a new human mutation assay that identifies mutant white blood cells that have lost the normal function of the gene that produces HLA-A, a cell surface protein. The assay yields two types of information about *in vivo* or *in vitro* mutations: the mutation frequency associated with exposure to a chemical, and the types and frequencies of mutations found, i.e., point mutations in the HLA-A gene, deletions from, or chromosome-wide mutations such as mitotic recombination. The information from the assay can be used in a simple direct way for exposure assessment, and can also be used in the PBPK-cancer model for risk assessment. Efforts in FY 1991 have been directed toward setting up the assay and beginning to gather mutation frequency data on smokers. Preliminary results

indicate an increase in mutation frequency at the HLA-A locus which is much higher than at other genes. Thus, the assay may greatly increase our ability to assess cancer risks posed from low level exposures such as environmental tobacco smoke.

In summary, this work, although preliminary in many respects, has clearly indicated that biologically-based risk assessment is both feasible and useful. This collaborative research is continuing with follow-up funding from the Environmental Protection Agency under a Superfund Center and the Food and Drug Administration.

Publications

Journals and Proceedings

F.Y. Bois and D.G. Paxman, "An Analysis of Exposure Rate Effects for Benzene Using a Physiologically-Based Pharmacokinetic Model." *Regulatory Toxicology and Pharmacology*, in press, LBL-31349 (1991).

F. Bois, M. Smith, and R. Spear, "Mechanisms of Benzene Carcinogenesis: Application of a Physiological Model of Benzene Pharmacokinetics and Metabolism," *Toxicol. Lett. 56*, 283 (1991).

F. Bois, T. Woodruff, and R. Spear, "Comparison of Three Physiologically-Based Pharmacokinetic Models of Benzene Disposition," *Toxicol. Appl. Pharmacol. 110* (1), 79 (1991).

P.J.E. Compton, K. Hooper, and M.T. Smith, "Human Somatic Mutation Assays as Biomarkers of Carcinogenesis." *Environ. Health Perspectives 94*, 135 (1991).

R. Spear, F. Bois, T. Woodruff, D. Auslander, J. Parker, and S. Selvin, "Modeling Benzene Pharmacokinetics: Calibration and Parametric Sensitivity Across Three Sets of Animal Data," *Risk Anal. 11*(4), 641 (1991).

Administration. The model was parameterized using *in vitro* and *in vivo* experimental data on benzene toxicokinetics and metabolism.

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F. Bois, M. Smith, and R. Spear, "Mechanisms of Benzene Carcinogenesis: Application of a Physiological Model of Benzene Pharmacokinetics and Metabolism," *Toxicol. Lett. 56*, 283 (1991).

F. Bois, T. Woodruff, and R. Spear, "Comparison of Three Physiologically-Based Pharmacokinetic Models of Benzene Disposition," *Toxicol. Appl. Pharmacol. 110* (1), 79 (1991).

P.J.E. Compton, K. Hooper, and M.T. Smith, "Human Somatic Mutation Assays as Biomarkers of Carcinogenesis." *Environ. Health Perspectives 94*, 135 (1991).

R. Spear, F. Bois, T. Woodruff, D. Auslander, J. Parker, and S. Selvin, "Modeling Benzene Pharmacokinetics: Calibration and Parametric Sensitivity Across Three Sets of Animal Data," *Risk Anal. 11*(4), 641 (1991).

Cell and Molecular Biology Division

Protooncogenes and Tumor Suppressor Genes in Normal and Transformed Growth Control

Principal Investigator: Judith Campisi

Funding: $147, 200

Project Description

The overall aim of this project was to understand, at a molecular level, how growth and differentiation are coordinated in normal cells and how these processes become dissociated in tumor cells. Protooncogenes and tumor suppressor genes are known to be critically important in regulating the proliferation of normal cells; in tumor cells, one or both classes of genes are invariably altered. It was proposed to study (1) the ability of the primary (normal) and transformed type 2 cells to express genes that are known to be important in cell proliferation and differentiation and (2) the proliferative capacity of normal chick embryo fibroblasts, and the effects of the c-src cellular protooncogene on the growth and differentiated properties of these cells.

Accomplishments

The project focused primarily on the growth and differentiation of rat lung aveolar type 2 cells. Primary type 2 cells were transformed with a well-characterized oncogene — the large T antigen of the SV-40 virus. T antigen is a potent and multifunctional viral oncogene that acts, in part, by inactivating at least two cellular tumor suppressor genes. Results of the studies indicate that transformation by T antigen, directly or indirectly, activates a protooncogene important in cell proliferation (c-fos), represses a differentiation-specific gene (keratin), and induces a gene associated with cells having a high proliferative capacity (vimentin). By microinjecting T antigen genes directly into primary cells, it was determined that c-fos, but not keratin or vimentin, was under the direct control of T antigen. Moreover, the ability of T antigen to activate c-fos was independent of its ability to inactivate the retinoblastoma tumor suppressor gene. Thus, transformation by oncogenes such as T antigen may proceed in two steps: activation of growth-associated genes may be the first and immediate step, whereas alterations in differentiation-associated genes may, in turn, be effected by one or more growth associated gene, such as c-fos.

The studies on the proliferative capacity of normal chick embryo fibroblasts found that primary chick embryo fibroblasts could be passaged for approximately 20 passages before the cultures reached senescence (i.e., the limit of their proliferative lifespan). Moreover, preliminary data suggest that src transformation did not affect the proliferative lifespan of the cells, although the cells acquired a number of other features characteristic of tumor cells (e.g., reduced requirements for growth factors and cellular adhesion, increased glucose uptake, refractory appearance, decreased extracellular matrix production, etc.). These studies provide a molecular framework for understanding how growth and differentiation are altered during carcinogenesis.

Calcium Signal Transduction during Human Mammary Carcinogenesis

Principal Investigator: Paul Yaswen

Funding: $75,000

Project Description

Studies in numerous laboratories have implicated changes in signal transduction of growth or differentiation factors in the process of neoplastic transformation. Calcium has been shown to be a key regulator of cellular growth and differentiation in epithelial cells derived from tissues such as skin and breast. Many tumor cell lines have reduced requirements for Ca^{+2} and are unable to differentiate in response to elevated Ca^{+2} levels. Calmodulin is a protein that is thought to be a primary mediator of cellular responses to Ca^{+2} fluxes. Recently, the expression of a gene encoding a protein very similar yet distinct from calmodulin has been found to be

altered after tumorigenic transformation of certain epithelial cells. Levels of mRNA for this protein, designated NB-1, are downregulated in tumorigenically transformed human mammary epithelial cells (HMEC) with respect to their closely related normal counterparts. The present studies have been initiated to learn more about the NB-1 protein and how absence of this regulatory molecule might contribute to the tumorigenic phenotype.

Accomplishments

Experiments utilizing purified recombinant NB-1 protein and antiserum specific for NB-1 protein have shown that despite the shared identity of 85% of their 148 amino acids, calmodulin and NB-1 protein are easily distinguished. Polyclonal antibodies raised against NB-1 recognize a protein that is abundant in cultured normal human mammary epithelial

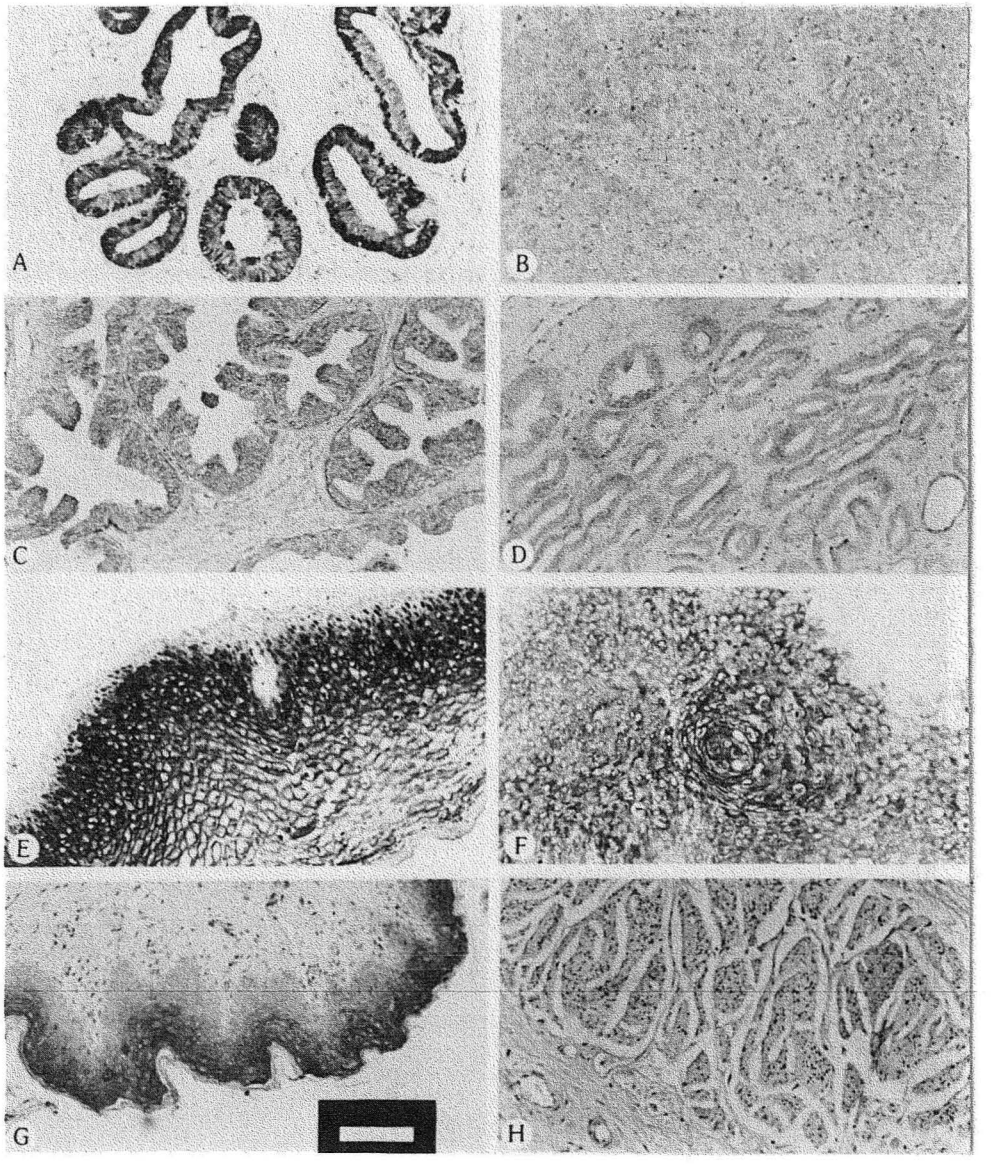

Figure 1. Immunohistochemical demonstration of NB-1 protein in normal and neoplastic human epithelial tissues: (A) normal breast; (B) breast carcinoma; (C) normal prostate; (D) prostate carcinoma; (E) normal cervix; (F) squamous carcinoma of the cervix; (G) normal foreskin; (H) epidermoid carcinoma of the cervix. (CBB 910-7947)

cells, but which is absent or barely detectable in fibroblasts or tumor cell lines. Calmodulin, in contrast, is expressed at relatively invariant levels in all cells, normal and transformed. The immunohistochemical distribution of NB-1 protein in histologically normal tissues suggests that expression of the gene is regulated during epithelial differentiation (see Figure 1).

The majority of a small number of malignant tissues examined had lowered or undetectable NB-1 expression relative to normal tissues. Lowered NB-1 expression in tumors may result from alterations in the proportions of cell types of different differentiation states. These alterations could be a direct result of malignant transformation, or a necessary precondition for carcinogenesis to proceed. Experiments are currently planned to determine whether expression of the NB-1 protein is responsible for maintaining specific differentiated traits in normal epithelial cells and whether NB-1 expression is incompatible with growth of certain tumor cells. This research will hopefully lead to a better comprehension of theregulatory influences that govern epithelial cell behavior and may ultimately lead to novel therapeutic approaches for the treatment of cancer.

Publications

Other Publications

P. Yaswen, A. Smoll, J. Hosoda, G. Parry, and M.R. Stampfer, "Protein Product of a Human Intronless Calmodulin-like Gene Shows Tissue-specific Expression and Reduced Abundance in Transformed Cells," submitted for publication (1991).

M.R. Stampfer, P. Yaswen, G. Parry, and J. Hosoda, "An In Vitro Human Mammary Epithelial Model System for Studies of Differentiation and Carcinogenesis," in *Neoplastic Transformation in Human Cell Systems In Vitro*, eds. J.S. Rhim and A. Dritschilo, Humana Press, Totowa, NJ, p. 259–267 (1991).

M.R. Stampfer and P. Yaswen, "Factors Influencing Growth and Differentiation of Normal and Transformed Human Mammary Epithelial Cells in Culture," in: *Transformation of Human Epithelial Cells: Molecular and Oncogenetic Mechanisms*," ed. G.E. Milo, CRC Press, in press (1991).

Chemical Biodynamics Division

Novel Fluorescent Probes from Nucleic Acid-Dye Complexes

Principal Investigators: Alexander N. Glazer and Richard A. Mathies

Funding: $54,100

Project Description

The proposed research rested on two parallel developments. First, a novel laser-excited confocal fluorescence gel scanner was developed to detect fluorescently labeled DNA fragments on agarose and acrylamide gels. Second, the principal investigators established that the fluorescent bis-intercalator, ethidium homodimer (EthD), formed complexes with double stranded (ds) DNA stable to electrophoresis. The high sensitivity of the detection system coupled with the ability to form dsDNA-fluorescent dye complexes that carry hundreds of chromophores, and absence of free dye, allowed detection of DNA fragments at sensitivities over 100-fold higher than by previously available fluorescence methods. Further work was undertaken to examine complexes between DNA and fluorescent bis-intercalating dyes other than EthD to establish the generality of the observations made with the latter compound and to design and build a simultaneous two-color scanner for concurrent acquisition of data from two different fluorophores. The ultimate objectives of this work are to develop methods for high sensitivity multiplex mapping of DNA restriction digests to facilitate ordering of cosmid clones, identification of microsatellite DNAs, detection of products of amplification by the polymerase chain reaction, etc., and to prepare a family of distinctive DNA-fluorescent dye complexes to use as probes in applications such as fluorescent in situ hybridization on chromosomes, or immunoassay applications.

Accomplishments

In a continuation of the studies of dsDNA-intercalation complexes, it was shown that complexes stable to electrophoresis were formed with the unsymmetrical cyanine dyes thiazole orange dimer (TOTO; 1,1'-(4,4,7,7-tetramethyl-4,7-diazaundecamethylene)-bis-4-[3-methyl-2,3-dihydro(benzo-1,3-thiazole)-2-methylidene]-quinolinium tetraiodide) and oxazole yellow dimer (YOYO; an analogue of TOTO with a benzo-1,3-oxazole in place of the benzo-1,3-thiazole). These complexes have particularly favorable properties for high sensitivity detection of dsDNA. Whereas the free dyes are virtually nonfluorescent in aqueous solution, both TOTO and YOYO show a fluorescence enhancement of over 2,000-fold upon binding to dsDNA. The fluorescence emission maxima of dsDNA complexes with YOYO and TOTO lie at 510 nm and 530 nm, whereas the dsDNA-EthD complex fluoresces maximally at 620 nm. All of these complexes can be efficiently excited at the 488 nm argon ion laser line. Simultaneous acquisition of data at two wavelengths was made possible by the construction of a two-color simultaneous scanner. Using mixtures of dsDNA-YOYO (or dsDNA-TOTO) complexes and dsDNA-EthD complexes, two-color detection of dsDNA was accomplished in a single lane in agarose gels with picogram sensitivity, and this methodology allows the determination of sizes of dsDNA fragments from 600 bp to 25 kbp with higher precision than reported.

These studies demonstrate the feasibility of preparing a panel of diverse stable highly fluorescent dsDNA intercalation dye complexes. These complexes have already proved valuable in the detection and sizing of dsDNA fragments. Future research will focus on the application of these complexes as fluorescent probes for the detection of other molecules.

Publications

Journals and Proceedings

M.A. Quesada, H.S. Rye, J.C. Gingrich, A.N. Glazer, and R.A. Mathies, "High-Sensitivity DNA Detection with a Laser-Excited Confocal Fluorescence Gel Scanner," *BioTechniques 10*, 616 (1991).

H.S. Rye, M.A. Quesada, K. Peck, R.A. Mathies, and A.N. Glazer, "High-Sensitivity Two-Color Detection of Double-Stranded DNA with a Confocal Fluorescence Gel Scanner Using Ethidium Homodimer and Thiazole Orange," *Nucleic Acids Research 19*, 327 (1991).

H.S. Rye, S. Yue, M.A. Quesada, R.P. Haugland, R.A. Mathies, and A.N. Glazer, "Picogram Detection of Stable Dye-DNA Intercalation Complexes with a Two-Color, Laser-Excited Fluorescence Gel Scanner, Methods in Enzymology," *Recombinant DNA*, Part H, R. Wu, Ed., in press.

Chemical Sciences Division

Molecular Beam Threshold Time-of-Flight Spectroscopy of Rare Gas Atoms

Principal Investigator: David A. Shirley

Funding: $43,200

Project Description

This project uses synchrotron radiation to conduct spectroscopic measurements on rare-gas atoms. This effort will contribute to the quantitative understanding of electron-electron correlation in highly-excited states, elucidation of the three-body problem in important prototype atoms, and determination of the structure of continuum states in which two-electron resonances are embedded.

A chamber was designed by John Allman of the CSD High Energy Chemical Physics Group, which incorporated supersonic molecular beam source, a beam catcher, and a differentially-pumped threshold electron analyzer. It also accommodated an ion yield spectrometer that was provided by the U. Becker Group of the Fritz Haber Institute, Berlin, and was mounted on the FU Berlin SX 700 II beamline of the Kaindl Group, FU Berlin. This chamber was manufactured at UCB/LBL and tested at LBL prior to shipment to Berlin. Mr. Allman traveled to Berlin, arriving with the chamber and was joined later by Dr. Tobias Reich and Mr. Barry Petersen of this group.

The plan was to collaborate with the Becker and Kaindl groups in studying rare gas atoms, beginning with helium, by collecting several different kinds of spectra simultaneously: photoionization, ion yield, and threshold photoemission. Of these, the photoemission spectra would be by far the most challenging and probably the most valuable as well. To maximize the chances for success, the supersonic molecular beam source was the interaction region between the crossed photon and atomic beams, and the run was scheduled during "single bunch" running time, a two week period in May, because of the time-of-flight (TOF) requirement of the detector.

Accomplishments

The molecular beam source was completed and transported to Berlin, where it was mounted together with equipment from the Becker Group of the Fritz Haber Institute on the Free University of Berlin SX700/II beamline at BESSY and used in a "single bunch" run during two weeks in May and June 1991. Several difficulties were overcome to perform the experiment.

The apparatus was successfully assembled. It held a very good vacuum, in the 10^{-10} range, and the (innovative) thin window design was successful. After the adjustment the TOF detector worked, and first experiments were tried on argon. Each step of the experiment was carried through to completion, and all components appeared to be in working order — a triumph in itself, considering the large number of new components. In particular, the electron energy resolution appeared to be improved as hoped, although it was not practical to close the monochromator slits enough to quantify this result. The group was not able to obtain any final data, however, because the counting rate was disappointingly low, and attempts to improve it were unsuccessful.

The final conclusion was that a more intense light source will be needed in order to carry out this experiment successfully.

Technical Evaluation of Beamlines and Experimental Stations for Chemical Dynamics Applications at the ALS

Principal Investigators: Yuan T. Lee and Andrew H. Kung

Funding: $110,500

Project Description

The high brightness and high flux of photons that are becoming available from next-generation synchrotron sources offer new and exciting possibilities for gas-phase chemical physics studies. The goal of

this project was to perform a detailed evaluation of various synchrotron beamline technologies and examine improvements to synchrotron light output that would respond to specific needs of gas phase chemical research at synchrotron facilities. Specific objectives included numerical study of monochromator layout and choice of grating designs to achieve exceptionally high resolution of 1 part in 50,000 while maintaining a high throughput, and feasibility evaluation and design of high-order suppressor to achieve spectral purity of 1 part in 100,000 in undulator output for the applications.

Bend magnet and undulator beamline arrangements using normal incidence monochromators were studied by numerical ray tracing to obtain detailed focusing characteristics of each optical design option. The results were an optimized design that met the conditions: (1) at the specimen center, the width of the undulator beam spot in the horizontal direction must be kept extremely small, (2) the height of the beam from the floor should be 1.5 m, and (3) an identical monochromator design would be adapted for the bend magnet beamline and the undulator beamline. Various options for the approach to grating design have been examined critically. The merits of ruled gratings, variable spaced gratings, and holographic gratings were compared. Scientific, technical, and economic trade-offs were carefully evaluated and resulted in a final design recommendation.

Of importance was to target and achieve spectral purity of 1 part in 100,000. A number of options were examined. The criteria used for evaluation were high throughput, broad and continuous tunability, cost, compactness, and compatibility with the experiments. Options were studied quantitatively and in conjunction with the optics arrangement of the beamlines. Results led to a highly optimized gas filter design for the purposes of chemical dynamics research at synchrotron sources.

Accomplishments

Capability for doing ray-tracing of optical designs for the bend magnet beamline and for the undulator beamline has been developed. Ray-traced spot diagrams and line profiles are constructed for three monochromator designs using a 10 μm slit width and equipped with a conventional grating, a holographic grating, or a ruled grating switch variable spacing and curved grooves. The ruled grating with variable spacing and curved grooves provides the most satisfactory results, with both coma and astigmatism well corrected. The results show a spectral resolving power of 90,000 over a wavelength range of 0 to 200 nm. It is therefore possible to meet the stringent requirements of gas phase chemical dynamics applications. However, there is only one supplier of a grating with variable spacing and curved grooves. A holographic grating gives a factor of two to three wider line width at the specimen center. In situations where this can be tolerated, the holographic grating may be the best compromise for the sake of its easier availability. The overall beamline design has also been examined. In addition to the monochromator optics, the design incorporated use of toroidal mirrors to refocus the exit beam to create an intermediate focus to accommodate a high order suppressor on the undulator beamline.

High order suppression of undulator light is studied in detail. It is discovered that a combination of reflection filtering and rare gas filter will provide a spectral purity of better than 1 part in 100,000 for the energy range of 5-30 eV. Reflection filter composes of using normal incidence and slightly off-grazing incidence metal mirrors in the beamline that cuts off all the photons with energy higher than 30 eV. The rare gas filter then serves to eliminate the unwanted low orders from the undulator emission. A molecular beamless gas filter is designed. The filter has an active length of 10 cm, using up to 30 Torr of rare gas. The filter is enclosed in a compact, triply differentially pumped chamber. Molecular beam chokes and side vents are incorporated to prevent gas streaming into the synchrotron source or the experiment. A baseline pressure of 3 nanoTorr can be achieved. This pressure is compatible with the residual gas pressure in the beamline vacuum. Presence of filter also will prevent corrosive gas molecules that will be used in the experiment from getting to the beamline optics and storage ring section. As a follow-on extension of this project, funding has been received from the Department of Energy to construct and test a prototype of this high-order suppressor for the purpose of evaluating its efficacy at the ALS.

Earth Sciences Division

Displacement Detectors for Seismometry

Principal Investigators: Thomas V. McEvilly, William F. Kolbe, Joseph E. Katz, and Martin J. Pollard

Funding: $59,300

Project Description

An inertial seismometer in its simplest form consists of a mass suspended elastically against gravity from a frame attached to the earth's surface. The relative motion of the mass with respect to the suspension frame is a measure of the acceleration of the ground. Because of nonlinearities and other spurious behavior, the dynamic amplitude and frequency range of such an instrument is limited. Significantly improved performance can be obtained if the output of the displacement transducer is amplified and fed back to the suspended mass through a force transducer. Under the conditions where the loop gain is large, the system response is then dominated by the generally more stable and well-characterized electronic components in the feedback loop. A seismometer can, in principle, be constructed of components of any size range. For example, similar performance should be possible with a pendulum of short period, high Q and high displacement resolution or a pendulum with a long period, and lower Q and lower displacement resolution. Most seismometers of small physical dimension have the advantage of portability, increased freedom from spurious vibrational modes, and potentially lower cost. On the other hand, they require displacement transducers of very high sensitivity. In this research, we investigate the development of miniaturized accelerometers employing state-of-the-art displacement detection methods and microfabrication techniques to determine if adequate sensitivity and dynamic range for seismometry can be achieved.

The development of displacement detectors of high sensitivity is an area of research that has received considerable attention in the fields of Scanning Tunneling Microscopy (STM) and Atomic Force Microscopy (AFM), and the generation and measurement of sub-angstrom motions have become more or less routine. At the same time, developments in semiconductor device fabrication technology have made it possible to produce freestanding microstructures such as cantilevers and other devices with great precision on silicon substrates. These techniques are applied to accelerometer development. The approach is to construct a model using existing devices testing the various concepts in the initial stages of the project, with the development of an integrated product during the second year. The plan is to complete design limitation calculations, to establish "on-paper" specifications that appear to be reachable, and to fabricate several test devices and evaluate their performance. The goal will be to determine if miniaturized accelerometers with performance specifications adequate for seismometry can be developed. If results are positive, the plan is to reduce the design to a silicon-based, integrated circuit model and to measure its performance.

Accomplishments

Investigation of the limiting noise/sensitivity factors in the application of novel displacement detectors has developed in the fields of Scanning Tunneling Microscopy and Atomic Force Microscopy. Sub-angstrom displacement sensitivities (10^{-4} Å/ $\sqrt{\text{Hz}}$) demonstrated in microscopy appear to offer a route to a revolutionary advance in terms of miniaturization and simplicity for seismometry. Initial work in FY 1991 has established the state-of-the-art as explored in other laboratories (Caltech/JPL are looking at the concept), and the basic calculations of displacement sensitivity have been completed. It is clear that, while basic device sensitivities are very good, the physical constraints faced in incorporating them into an inertial accelerometer call for sensitivities at least as good as the above value and introduce formidable thermal noise problems that must be addressed.

Advancement of Fault Assessment Techniques and Improving Estimates of Seismic Risk at LBL

Principal Investigator: Patrick L. Williams

Funding: $69,100 (FY 91)
$74,800 (FY 90)

Project Description

This project is directed at advancing fault assessment techniques through new studies of Hayward fault neotectonics. Highlighted are detailed studies of small and large scale sedimentary basins and their unique potential to reveal detailed sedimentary records of fault paleoseismicity and the kinematics of basin inception and growth. Research of Hayward fault paleoseismicity has yielded data on the nature and timing of several past ruptures of the Hayward fault.

The Hayward fault produced two large earthquakes in the 19th century and thus is a key focus of concern with respect to the imminence of future damaging earthquakes. No opportunity for direct measurement of the frequency of Hayward fault ruptures had been recovered prior to this study. Furthermore, the fault's slip rate and segmentation remain relatively poorly known. Inferences of the fault's recurrence behavior[1] required assumptions to be made about segmentation, frictional properties, slip rate, and characteristic seismogenic displacement. Uncertain knowledge of these parameters argues that any current estimates of recurrence behavior be regarded with caution. Research outlined here recovers direct geological measurements of past recurrence behavior. These measurements provide critical testing of a number of assumptions made in the 1990 Working Group analysis of Hayward fault rupture hazard.

Shallow subsurface profiling across the major East Bay fault zones (Hayward, Concord - Green Valley, and Antioch faults) was a focus of the Bay Area Seismic Imaging experiment (BASIX) field study. Over 200 kilometers of high-resolution profiling were completed during the initial BASIX cruise and during a subsequent cruise devoted solely to high-resolution profiling. The high-resolution data have allowed us to construct new maps of remarkable deformation features within the upper 5 to 150 meters of sedimentary material. Geological structure imaged in the high-resolution exercise include several folds and faults that heretofore were unknown.

The initial BASIX high-resolution data were recorded on the S.P. Lee using a four-plate Uniboom system. Those data were recorded on graphic recorders and analog tape. A second high-resolution BASIX cruise was conducted by the USGS research vessel David Johnston (DJ). Use of the DJ provided access to shallower water (3-ft draft), allowing us to substantially increase the area of high-resolution track coverage. A single plate Geopulse system and a 5 cubic inch air gun were alternately deployed on the second cruise. Single channel reflection data from both sources were recorded digitally.

Accomplishments

Evidence of the timing of Hayward fault slip over the past 1800 years has been recovered in excavations near Mowry Street (the "Mowry site") in Fremont. Recurrent motion of the fault is recorded by offset, tilt, and liquifaction of late Holocene pond and fluvial deposits at the northern end of Tule Pond (Figure 1). The pond is contained in a 100-m-wide pull-apart graben cut into the Holocene alluvial fan complex of Alameda Creek. The pond is fault-bounded on the west and east. During 1990 and 1991 five trenches were excavated across the eastern trace, revealing evidence for five Hayward fault ruptures in the past 1800 years. Significant gaps were also identified in the sedimentary record, thus some late Holocene ruptures are almost certainly not recorded at this site.

The two latest ruptures identified (events R and U) are recorded by 19° and 9° tilts of successive pond strata and tilting of a channel filling deposit by 19°. Strata across the length of trenches M1 and M2 were folded in a monocline with a vertical amplitude of 2 to 2.5 m during this period. The earliest calendar age of the youngest unit deposited prior to events R and U, the channel fill, is AD 1680. If event U is the 1868 event, this indicates the maximum renewal time is on the order of 190 years. While this record continues to require corroboration and development, it represents the only known data on the timing of the Hayward rupture prior to the about 150-year period of local historical record.

The goals of the high resolution studies in BASIX included investigation of the pattern of deformation around the Hayward - Rogers Creek fault step and

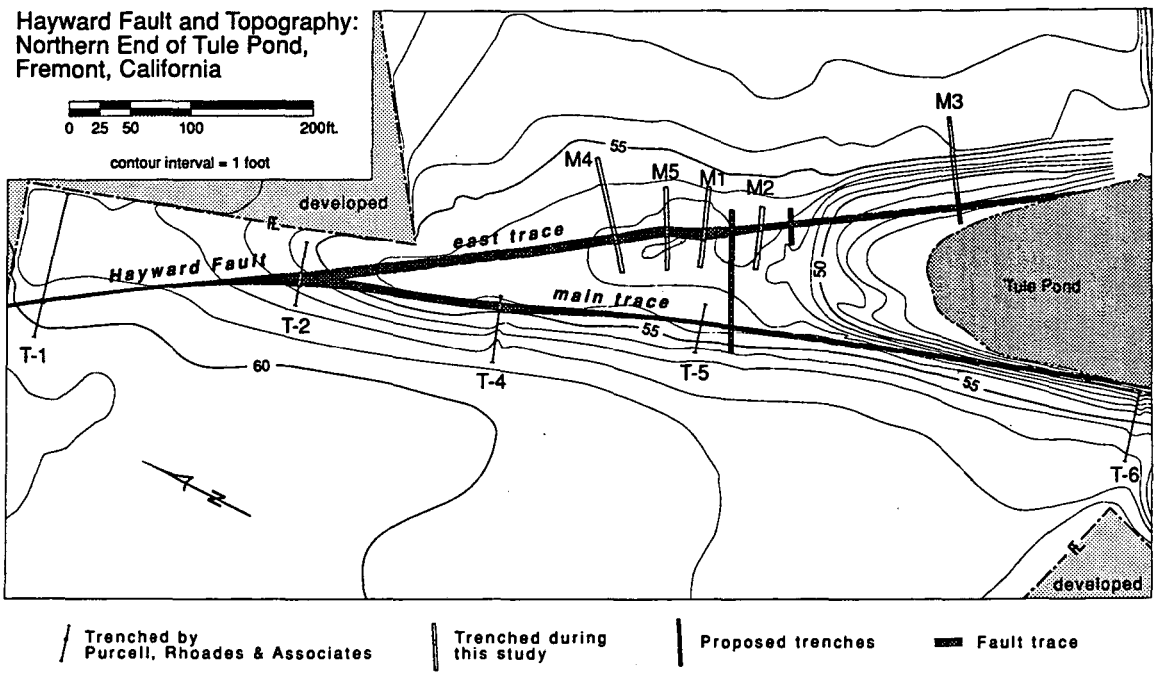

Fig. 1. Orthometric map of Mowry site and locations of trenches M1 - M5. Map shows the topographic expression of the northern end of the Tule Pond graben. The graben results from extension across a right double-bend of the west trace.

imaging of the position of the controversial "Antioch fault." Initial interpretations of the high-resolution data suggest the following conclusions: (1) A prominent fault was discovered in eastern San Pablo Bay, possibly linking the Rogers Creek and Pinole faults. The fault is located on the west side of a broad west-dipping Plio-Pleistocene (?) monocline. (2) The Antioch fault may not exist at its presently mapped location, but a significant active structure does appear to be expressed by a sharply defined west-dipping monocline and associated faulting 5.5 km farther west, near Pittsburgh. The "Pittsburgh fault" coincides with a clear NNW trending group of deep earthquakes.

Reference

1. Working Group: J.H. Dietrich, C. R. Allen, L.S. Cluff, C.A. Cornell, W.L. Ellsworth, L.R. Johnson, A.G. Lindh, S.P. Nishenko, C.H. Scholz, D.P. Schwartz, W. Thatcher, P.L. Williams, "Probabilities of Large Earthquakes in the San Francisco Bay Region," California, USGS Circ. 1053, 51pp. (1990).

Publications

Journals and Proceedings

P.L. Williams, P. Holland, M. Wopat, and F. Yeates, "Preliminary Evidence of Hayward Fault Paleoseismicity," EOS Trans. AGU 71, 1560 (1990).

P.L. Williams, "Evidence of Late Holocene Ruptures, Southern Hayward Fault," California, GSA Abstracts with Programs, Spring 1991 SSA/GSA-Cordilleran meeting.

R.J. Anima and P. L. Williams, "High-Resolution Marine Profiling in BASIX: Complex Structures at Major East Bay Faults," EOS Trans. AGU 72, 446 (1991).

Materials Sciences Division

Semiconductor Thin Films Using Nanocrystals Precursors

Principal Investigator: Paul Alivisatos

Funding: $71,200

Project Description

The efficacy of using nanocrystals as precursors to thin film growth is being pursued.

Accomplishments

It has been determined that nanocrystals of many common semiconductors, including GaAs and CdS, melt at temperatures well below the bulk melting point. In these experiments, nanocrystals are deposited at low density on an amorphous carbon substrate, the temperature of which can be controlled. Using the facilities at the National Center for Electron Microscopy, the nanocrystal electron diffraction pattern is collected as a function of temperature. At the melting temperature, we find that the diffraction pattern disappears abruptly, but is recovered upon cooling. The melting temperature determined in this way is an extremely strong function of nanocrystal size. For instance, 24 Å diameter CdS nanocrystals melt at 580 K, compared to a bulk melting temperature of 1750 K. At high nanocrystal coverage, the particles fuse and form thin films.

At the same time a method has been developed for attaching nanocrystals to metal or semiconductor surfaces, using organic molecules as tethers to explore whether it is possible to grow thin films of semiconductors using these complete assemblies. This would make it possible to grow thin films of semiconductors at uncommonly low temperatures using nanocrystals as precursors.

Publications

Journals and Proceedings

V.L. Colvin, A.P. Alivisatos, and J.G. Tobin, "Valence-Band Photoemission from a Quantum Dot System," *Phys. Rev. Lett.* ***66***, 2786 (1991).

J.G. Tobin, V.L. Colvin, and A.P. Alivisatos, "Photoemission Investigation of Compound Semiconductor Monodisperse Clusters," *J. Vac. Sci. Tech. A* ***9***, 852 (1991).

M.A. Olshavsky, A.N. Goldstein, and A.P. Alivisatos, "Organometallic Synthesis of GaAs Crystallites Exhibiting Quantum Confinement," *J. Am. Chem. Soc.* ***110***, 9438 (1990).

A.N. Goldstein, C.M. Echer, and A.P. Alivisatos, "Melting in Semiconductor Nanocrystals," submitted to *Science.*

V.L. Colvin, A.N. Goldstein, and A.P. Alivisatos, "Semiconductor Nanocrystals Covalently Bound to Metal Surfaces," submitted to *J. Am. Chem. Soc.*

A.N. Goldstein, V.L. Colvin, and A.P. Alivisatos, "Observation of Melting in 30 Diameter CdS Nanocrystals," *Mater. Res. Soc. Symp. Proc.* ***206***, 271 (1991).

Quantum Size Effect in Semiconductor Nanostructures

Principal Investigator: Daniel S. Chemla

Funding: $346,100

Project Description

The optical properties and the dynamics of elementary excitations of gallium arsenide quantum wells under very high magnetic fields are being investigated.

Recent advances in modern crystal growth techniques have resulted in the fabrication semiconductor thin films of very high quality with atomic-layer control of the thickness. These novel artificial materials have had a tremendous impact on the fundamental sciences of solid state and have already produces numerous applications. The proposed research has a goal to extend these investigations to quasi-zero and quasi-one dimensional systems and to understand the dynamics and relaxation of the electronic states with such reduced dimensionality.

The actual realization of structures with quasi-zero dimensionality has been plagued by the difficulties of obtaining samples with high interface quality and

small size fluctuation. To investigate the optical properties of quasi-0D and quasi-1D objects while avoiding the aforementioned difficulties, a large magnetic field perpendicular or parallel to the plane of a high-quality quantum well structure will be applied. In the absence of magnetic field, the e-h pairs are free to move along the plane of the quantum wells, but their motion perpendicular to it is restrained by the quantum well thickness, L_z. A perpendicular magnetic field, B, further confines the e-h pairs states in this plane within an area determined by the cyclotron radius, r_c, which for semiconductors such as gallium arsenide can be made smaller than the bulk exciton Bohr radius. In such a configuration it becomes possible to study by optical spectroscopy the *physics of the 2D $\longrightarrow$ 0D transition* in materials of high quality and without size fluctuation. Similarly by application of the field parallel to the plane of the layers the *physics of the 2D $\longrightarrow$ 1D transition* can be studied.

Furthermore, the recent advances in Ti:Sapphire-laser technology make it possible to envision highly reliable laser sources to deliver high power and high quality ultrashort pulses tunable in the vicinity of the fundamental gap of gallium arsenide. This type of laser will be used for performing femtosecond-time resolved spectroscopy of gallium arsenide quantum wells in large magnetic fields.

Accomplishments

During the first year of this program a state-of-the-art laboratory was set up with the facilities for investigating the optical properties and dynamics of elementary excitation of condensed matter at photon energies close to the band gap of gallium arsenide, i.e., 1.5 eV. A new Ti:Sapphire laser system has been built up to deliver 100 fs optical pulses at 100 MHz repetition rate and tunable between 750 nm and 900 nm. This laser has been amplified to mJ level by a copper-vapor laser pumped dye-amplifier, and the high energy pulses will be used to produce broad band light continuum covering the 500 nm – 1.3 μm spectral range with the same 100 fs duration at a repetition rate of 8 kHz. Preliminary experiments on gallium arsenide quantum wells in the absence of magnetic field have started. They include investigation of effects of Coulomb mediated exciton-exciton interaction on the time profile of the free induction decay of the photoexcited quantum wells. These experiments, designed for testing the apparatus and provide training to students, have already provided original and novel results that are being processed.

The specifications of an adequate low temperature split-coil magnet have been determined. The cryostat-magnet assembly should have four windows with capability of hosting optical lenses within the vacuum chamber as well as the flexibility of arbitrary orientation of the sample with respect to the magnetic field.

Superior Superconducting Materials

Principal Investigators: Marvin L. Cohen and Alex Zettl

Funding: $100,600

Project Description

The goal of this project has been to produce and study superconducting materials with interesting and desirable properties. Such properties include materials with tuned interplanar coupling interactions that might affect the superconducting transition temperature, critical current, mechanical strength, and dissipation in magnetic fields.

Existing classes of oxide superconductors are extremely sensitive to subtle changes in doping, pressure, structure, and oxygen configuration. Changing material parameters slightly can lead to compounds with highly modified transport and mechanical properties. It is by no means clear if the existing materials, in their "pristine" form, are optimized for all applications. For example, by slightly changing the interlayer coupling of a material, T_c may go down slightly, but the material may exhibit enhanced current-carrying capability.

The method in developing new superconducting materials based on oxide superconductors is a joint experimental/theoretical approach. Predictions for new structures, using stability arguments based on new theoretical pseudopotential radii methods, are used as a synthesis guide by M.L. Cohen's theory group. New materials are generated and characterized by various structural, transport, and mechanical measurements in A. Zettl's laboratory. The primary method of modifying existing oxide superconductor structures is to apply the technique of intercalation, where foreign atomic or molecular species are inserted into the lattice structure of the host material. This leads to changes in coupling parameters and possible charge transfer.

Accomplishments

This project has been successful in predicting and synthesizing new superconductors with novel properties. The materials form ideal prototypes for the study of mechanisms of high temperature superconductivity, and they hold promise for various device applications.

Intercalation has been demonstrated as a viable synthesis route for different classes of oxide superconductors. In particular, iodine guest species have been intercalated into host structures based on BiSrCaCuO. Iodine intercalates between the Bi-O sheets, dramatically increasing the c-axis dimension while decreasing the interplane Cu-O coupling. The intercalation technique has been demonstrated for the entire series of Bi-based high-T-superconductors, Bi-2212, Bi-2201, and Bi-2223. The highest T_c achieved is 100 K for Bi-2223. There is strong evidence that other atomic and molecular species can be intercalated into these and related high-T_c structures.

Different "stage" structures (i.e., nest in every host layer = stage 1, in every other layer = stage 2, etc.) have been synthesized, demonstrating that the intercalation process can be finely controlled, allowing a whole range of different structures to be synthesized for a given host and guest. For iodine in Bi-2212, stage structures ranging from stage 1 to stage 5 have been obtained and identified by x-ray and TEM studies (see Fig. 1).

The new materials allow basic parameters to be identified and mechanisms to be explored for high-T_c oxides. For example, the role of interplanar coupling to the high-T_c superconductivity mechanism has been identified (it contributes ~10 K to T_c in Bi-2212). Transport measurements on the new materials have ruled out various models on high-T_c superconductivity, such as those that rely on interplane tunneling that results in a 1/T-like temperature dependence to the out-of-plane resistance. There is also preliminary evidence that the current-carrying properties of the new materials have been enhanced with respect to those of the pristine host. From the modified structure of the new materials, it is likely that the elastic properties have been altered. Elastic measurements are in progress.

Several important instrumentation advances have also resulted from this study. In order to screen samples quickly, a novel low-field magnetometer has exceptional sensitivity and fast turnaround time. A contactless resistance probe has also been

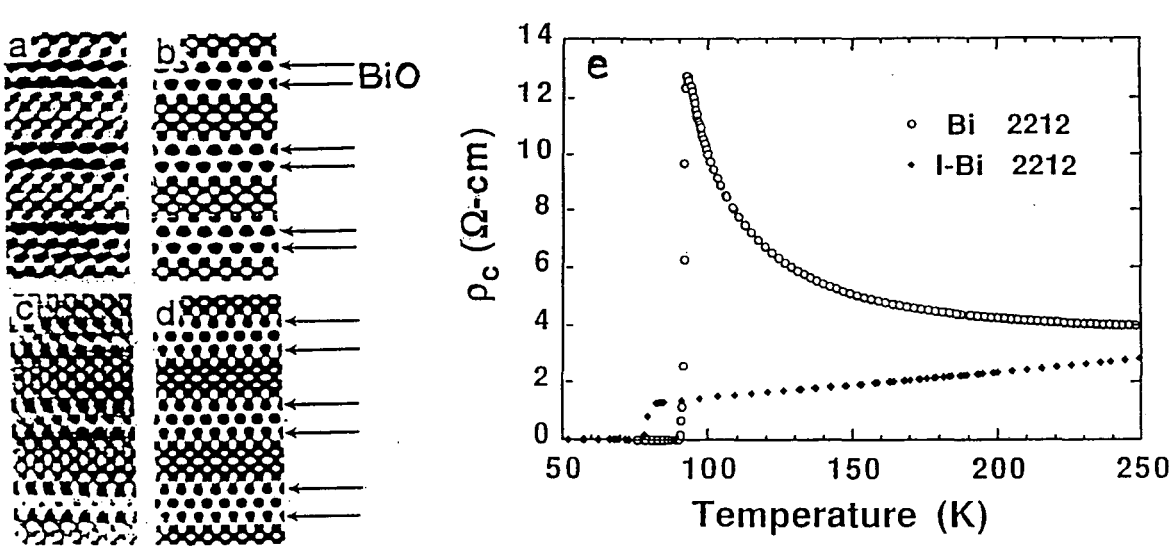

Fig. 1. Atomic resolution transmission electron microscope images of (a) pristine and (c) stage-1 iodine intercalated $Bi_2Sr_2CaCu_2O_x$. (b) and (d) show corresponding computer-generated images. (e) Shows dc c-axis electrical resistivity for pristine and intercalated specimens; note that intercalation results in a "metallization" of the resistivity. The TEM images were obtained in collaboration with R. Gronsky and N. Kijima of the Lawrence Berkeley Laboratory.

pioneered, which measures resistance versus temperature without the need for wire bonding to a (possibly reactive) specimen.

Publications

X-D. Xiang, S. McKernan, W.A. Vareka, A. Zettl, J.L. Corkill, T.W. Barbee, and M.L. Cohen, "Iodine Intercalation of a High Temperature Superconducting Oxide," *Nature 348*, 145 (1990).

N. Kijima, R. Gronsky, H. Endo, Y. Oguri, S. McKernan, and A. Zettl, "Microstructure of the High T_c Phase (T_c~111K) in the Sb-Pb-Bi-Sr-CaCu-O System," *App. Phys. Lett. 58*, 188 (1991).

N. Kijima, R. Gronsky, H. Endo, Y. Oguri, S. McKernan, and A. Zettl, "Superconductivity and Chemical Composition of the High-T_c Phase (T_c~111K) in the Sb-Pb-Bi-Ca-Cu-O System," *Jpn. J. Appl. Phys. 30*, L99 (1990).

X.-D. Xiang, A. Zettl, W.A. Vareka, J.L. Corkill, T.W. Barbee III, and M.L. Cohen, "Epitaxial Intercalation of the Bi-Sr-Ca-Cu-O Superconductor Series," *Phys. Rev. B 43*, 11496 (1991).

N. Kijima, R. Gronsky, X.-D. Xiang, W.A. Vareka, A. Zettl, J.L. Corkill, and M.L. Cohen, "Crystal Structure of Stage-1 Iodine-Intercalated Superconducting $IBi_2Sr_2CaCu_2O_x$," *Physica C181*, 18 (1991).

X.-D. Xiang, W.A. Vareka, A. Zettl, J.L. Corkill, T.W. Barbee III, M.L. Cohen, N. Kijima, and R. Gronsky, "Tuning High-T_c Superconductors via Multistage Intercalation," *Science 254*, 1487 (1991).

X.-D. Xiang, W.A. Vareka, A. Zettl, J.L. Corkill, M.L. Cohen, N. Kijima, and R. Gronsky, "Metallization of the Resistivity Tensor in $Bi_2Sr_2CaCu_2O_x$ through Epitaxial Intercalation," *Phys. Rev. Lett. 68*, 530 (1992).

Surface, Interface, and Nanostructure Studies Using Synchrotron Radiation in Combination with Other Probes

Principal Investigator: Charles S. Fadley

Funding: $193,900

Project Description

This project emphasizes developing new methods for the study of surfaces, interfaces, and nanostructures and applying these methods to novel surface morphologies that have been synthesized as part of the research. A principal focus has been on experimental characterization techniques utilizing synchrotron radiation, and a considerable amount of work has thus been aimed at making extensive use of next generation systems such as the Advanced Light Source (ALS). However, another aspect of the research involves combining synchrotron radiation measurements with either in situ or separate laboratory characterizations by other complementary techniques in unique ways.

The principal experimental methods used are photoelectron spectroscopy and photoelectron diffraction with high resolutions in both energy and emission angles, which together provide information on both the atomic geometries of surface species in different chemical or magnetic states and the valence electronic structure that binds them together. Another recent development is the analysis of photoelectron diffraction data by holographic methods; this promises to produce true three-dimensional images of near-surface structure. State-of-the-art equipment is available for performing such angle-resolved diffraction studies and a next-generation system that will operate principally at the ALS is being worked on. This new system will provide higher resolutions and higher data acquisition rates, and will permit

detecting all electrons at extremely high rates, as well as measuring spin-resolved spectra in studies of magnetic systems. Another instrument development underway is the combination of photoelectron diffraction and scanning tunneling microscopy, two highly 2-complementary surface structure probes, in one ultrahigh vacuum system. These two techniques will also be combined in the system for the ALS. An important component of the work is also the theoretical interpretation of photoelectron diffraction patterns and the development of more efficient and accurate methods of extracting accurate structural information from them. This involves unique computer codes for calculating diffraction patterns, as well as for holographically inverting these patterns to produce real-space images.

Accomplishments

Experimental and theoretical studies of the possibility of surface structure determinations from electron emission holography. The intriguing prospect of being able to use electron diffraction patterns above surfaces to determine surface atomic structures directly by holographic imaging methods is a very recent idea. The group is still one of only a few in the world working to assess the feasibility of this approach. The experimental studies of both a simple adsorbate system (S/Ni) and the semiconductors Si and Ge show that holographic images do indeed contain features associated with near-neighbor atoms. These images are distorted and shifted by anisotropic effects in the electron-atom scattering, but several methods have been suggested that have been demonstrated to improve image quality.

Development of an ultrahigh vacuum scanning tunneling microscope and application of it to metal-semiconductor interactions. In preparation for combining scanning tunneling microscopy with photoelectron diffraction and holography, construction of an ultrahigh vacuum STM has been computed. This system provides for in situ transfer of specimens from the STM to stations for either metal deposition, ion bombardment, or LEED/Auger characterization. As a first system of study with it, the interaction of Sn with Ge(111) was chosen and obtained high-quality images with atomic resolution for several types of structures including the clean c(2×8) surface, room-temperature-deposited Sn atoms and microclusters, and an annealed Sn/Ge structure that is very similar to the well-known (7×7) reconstruction on Si(111). These images furthermore contain several new structural elements not observed before: a new type of structure on the clean surface that coexists with the better-known c(2×8), a (5×5) structure that coexists with (7×7) for annealed Sn/Ge, and the indication that Sn preferentially occupies adatom positions in the (5×5) and (7×7) structure that are away from the large corner holes of the unit cell. This work is presently being written up for publication.

Other surface structure studies based upon photoelectron diffraction. The controversial !3 × !3 structure of Ag on Si(111) is being studied, for which a detailed analysis of data obtained both in the laboratory and with synchrotron radiation is just being completed. Photoelectron diffraction has also been used to study a high-temperature surface phase transition on Ge(111) occurring 150° below the melting point. These results include holographic analyses below and above the transition temperature, and they indicate that the transition involves a layer at least 3–5 atoms thick, a conclusion that has further clarified the nature of what appears to be a surface "pre-melting" transition. Diffraction of inelastic photoelectrons has also been studied for Al, Ge, and W and found to be much suppressed along low-index directions due to multiple scattering effects that have been successfully modeled. Such effects could be useful in locating low-index directions in epitaxial layers. The diffraction of energy-integrated valence photoelectron spectra has been studied for W and found to exhibit both direct-transition effects (Brillouin zone selectivity) at lower temperatures, and atomic-orbital angular momentum effects for higher temperatures. Developing faster and more accurate methods continues for the theoretical simulation of photoelectron and Auger electron diffraction results. This work is centered on a general-purpose program for doing both single-scattering and fully-converged multiple-scattering calculations of such diffraction patterns. The approach is based on a new separable Green's function method due to J.J. Rehr of the University of Washington, who is a collaborator on this project. Another aspect of this work is the simulate spin-polarized photoelectron diffraction in both a single-scattering and multiple scattering framework collaborator, a direction that will be expanded. Finally, a general invited review of the present status of structure studies based upon both photoelectron diffraction and Auger electron diffraction has been completed.

Publications

Journals and Proceedings

B. Sinkovic, D.J. Friedman and C.S. Fadley, "Theory of Spin Polarized Photoelectron Diffraction," *J. Magnetism and Magnetic Materials, 92*, 301 (1991).

G.S. Herman and C.S. Fadley, "Inelastic Photoelectron Diffraction," *Phy. Rev. B, Rapid Commun. 43*, 6792 (1991).

S. Thevuthasan, G.S. Herman, R.S. Saiki, A.P. Kaduwela, and C. S. Fadley, "Electron Emission Holography: Prospects and Limitations," *Phys. Rev. Letters 67*, 469 (1991).

A.P. Kaduwela, D.J. Friedman, and C.S. Fadley, "Application of a New Multiple-Scattering Method to Photoelectron Diffraction and Auger Electron Diffraction," *J. Electron. Spectrosc. 57*, 223 (1991).

G.S. Herman, T.T. Tran, K. Higashiyama, and C.S. Fadley, "Valence Photoelectron Diffraction and Direct-Transition Effects," *Physical Review Letters* (in press): LBL-31733.

G.S. Herman, S. Thevuthasan, T.T. Tran, Y.J. Kim, and C.S. Fadley, "Imaging of Near-Neighbor Atoms in Semiconductors by Photoelectron Holography," *Physical Review Letters* (in press): LBL-31732.

S. Thevuthasan, G.S. Herman, A.P. Kaduwela, T.T. Tran, Y.J. Kim, R.S. Saiki, M.A. Van Hove, and C.S. Fadley, "Electron Emission Holography of Small Clusters and Surfaces," *Journal of Vacuum Science and Technology* (in press): LBL-31731.

B. Hermsmeier, B. Sinkovic, C.S. Fadley, M.O. Krause, J. Jiminez-Mier, P. Gerard, T.A. Carlson, S.T. Manson, "Energy Dependence of the Outer Core-Level Multiplet Structures in Atomic Mn and Mn-Containing Compounds, submitted to *Physical Review B*: LBL-31736.

R.S. Saiki, A.P. Kaduwela, and C.S. Fadley, "Structure Determination of c(2×2)S/Ni(001) by High-Resolution X-Ray Photoelectron Diffraction and Holographic Imaging," submitted to *Surface Science*: LBL-31734.

R.S. Saiki, A.P. Kaduwela, J. Osterwalder, D.J. Friedman, C.S. Fadley, and C.R. Brundle, "X-Ray Photoelectron and Low Energy Electron Diffraction Study of the Interaction of Oxygen with the Ni(001) Surface: c(2×2) to Saturated Oxide," submitted to *Surface Science*: LBL-31735.

A.P. Kaduwela, D.J. Friedman, Y. Kim, T. T. Tran, G.S. Herman, C.S. Fadley, J.J. Rehr, J. Osterwalder, H. Aebischer, and A. Stuck, "Multiple-Scattering Effects in Auger Electron Diffraction and Photoelectron Diffraction: Theory and Applications," Springer Series in Surface Science - The Structure of Surfaces III, Eds. S.Y. Tong, M.A. Van Hove, K. Takayanagi, and X.D. Xie, *Springer Verlag 24*, 77 (1991).

G.S. Herman, A.P. Kaduwela, T.T. Tran, Y.J. Kim, S. Lewis, and C.S. Fadley, "Inelastic Photoelectron Diffraction," Springer Series in Surface Science - The Structure of Surfaces III, Eds. S.Y. Tong, M.A. Van Hove, K. Takayanagi, and X.D. Xie, *Springer Verlag 24*, 85 (1991).

T.T. Tran, D.J. Friedman, Y.J. Kim, G.A. Rizzi and C.S. Fadley, "X-ray Photoelectron Diffraction Study of a High-Temperature Surface Phase Transition on Ge(111)," Springer Series in Surface Science - The Structure of Surfaces III, Eds. S.Y. Tong, M.A. Van Hove, K. Takayanagi, and X.D. Xie, *Springer Verlag 24*, 522 (1991).

G.S. Herman, A.P. Kaduwela, D.J. Friedman, M. Yamada, E.L. Bullock, C. Fadley, Th. Lindner, D. Ricken, A.W. Robinson, and A.M. Bradshaw, "Study of $(\sqrt{3} \times \sqrt{3})$ R30° Ag on Si(111) by Photoelectron Diffraction," Springer Series in Surface Science - The Structure of Surfaces III, Eds. S.Y. Tong, M.A. Van Hove, K. Takayanagi, and X.D. Xie, *Springer Verlag 24*, 600 (1991).

G.S. Herman, D.J. Friedman, C.S. Fadley, G. Granozzi, A. Rizzi, J. Osterwalder, and S. Bernardi, "X-ray Photoelectron Diffraction from the HgCdTe(111) Surface," *J. Vac. Sci. Tech. B9*, 1870 (1991).

Technical Assessment of New Methodologies for 1 Å Imaging Resolution in a Transmission Electron Microscope System

Project Investigator: Ronald Gronsky

Funding: $92,700

Project Description

The route to higher resolution performance in electron microscopes currently shows several divergent paths. Higher resolution can be obtained by higher accelerating potential, the method adopted this past year by several Japanese laboratories (Dr. H. Horiuchi at NIRIM, Tsukuba, and Dr. N. Uyeda at Kyoto, for example), and one in Europe (Dr. H. Seegar, Max Planck Institute, Stuttgart) at great expense, both monetary and in specimen integrity. High-voltage electrons are hostile to even the most densely-packed solids, causing severe irradiation damage that can alter the microstructure in unpredictable ways.

An alternative is based upon lower-voltage microscopy, utilizing the power of image processing and fast computational algorithms to extend resolution performance. This project has the goal of identifying the best low-voltage alternative to the damaging, higher-voltage route currently in vogue.

Accomplishments

Under this project, two theoretical studies have been pursued in parallel. One is the development of a method named "Extended Resolution Electron Microscopy" or EREM, that exploits preassigned focal settings for control of the pass bands in the contrast transfer function of the electron microscope. The resulting images are collected and summed in the computer with the net result that the final image has higher resolution. The second study involves the method of off-axis, holographic reconstruction employing a biprism in the intermediate image plane of the microscope to reconstruct an image with corrected complex phase information. Coding of the algorithms for holography has been completed using the object-oriented "C++" language in a window-driven and fully interactive environment. Another software package for the numerical postprocessing and image analysis of electron holograms has also been completed, containing procedures for all aspects of data analysis, from initial reduction of raw intensity measurements (either in the form of raw electron counts or in the form of a raster or photographic image) to noise reduction and aberration correction in the final image.

The first experimental assessment of the EREM method has only recently been completed, and some success has been achieved. Experimental assessment of the holographic reconstruction method is currently underway.

Terahertz Electrodynamics of Materials

Principal Investigator: Joseph Orenstein

Funding: $90,100

Project Description

Many of the most interesting and important phenomena in condensed matter physics are associated with energy scales in the terahertz (10^{12} Hz) regime. Coherent terahertz spectroscopy—the generation and detection of subpicosecond electrical pulses—promises to open this exciting regime for exploration. A unique facility which combines coherent terahertz spectroscopy with more conventional techniques is currently under development at Lawrence Berkeley Laboratory.

The availability of subpicosecond *optical* pulses has led to a detailed understanding of dynamical processes of materials with large gaps in the electronic density of states, i.e., semiconductors such as GaAs and Si. Similarly, subpicosecond *electrical* pulses will probe the dynamics of electronic systems that are either gapless or have much smaller gaps than typical semiconductors. Examples of great interest are disordered metals and superconductors, metals with naturally or artificially reduced dimensionality, and high-T_c superconductors. In many of these systems the timescale of the most important dynamical processes lies in the terahertz regime.

The application of coherent terahertz spectroscopy requires the generation, detection, and directed propagation of subpicosecond electrical pulses. The method to generate and detect subpicosecond electrical pulses is based on photoexcitation of a fast-response photoconductor such as radiation-damaged

silicon. The source (the detector is identical) consists of a coplanar transmission line deposited on top of the photoconductor. When the device is configured as a source, a dc bias of approximately 10 V is applied across the transmission line. Excitation of the photoconductor by an ultrashort optical pulse induces a current spike and launches a pulse down the line. If desired, the coupling of the pulse to free space is aided by an antenna structure. The same device is converted to a detector by connecting the transmission line to a current amplifier rather than a voltage source. Now the transmission line is biased by the electric field of the incident terahertz pulse, and a current proportional to this bias flows when a conductance path is provided by excitation of the photoconductor. The shape of the received pulse is measured by varying the time delay between the optical pulses that create and sample the pulse.

In addition to generation and detection a successful spectroscopy requires directed propagation of the radiation in order to measure the transmission or reflection coefficients of materials of interest. The two available modes of propagation are free space and transmission line. Free space is the ideal dispersive medium, and in principle may be used at all frequencies. At low frequencies, however, the study of mesoscopic scale materials is difficult because radiation cannot be focused to a spot smaller than the free space wavelength. Transmission lines allow radiation to be directed more precisely to small samples and extend the low frequency cutoff of the spectroscopy to approximately 10 GHz.

Accomplishments

Successful demonstration of generation, free space propagation, and detection of a terahertz beam has been accomplished. An illustration of the temporal profile of the transmitted electrical pulse, together with its Fourier transform, is shown in Figure 2 (a) and (b). As is apparent from the figures, the electrical pulse is extremely short, with useful frequency components that extend beyond one terahertz. The ratio of the peak height to the noise measured before the peak is greater than 4000, showing the potential for highly accurate measurements in the terahertz regime. The oscillatory structure in the time trace, which appears as sharp lines in the spectrum, results from absorption due to atmospheric water vapor.

The successful demonstration described above resulted from important progress made in each of the component parts of the spectrometer system. The

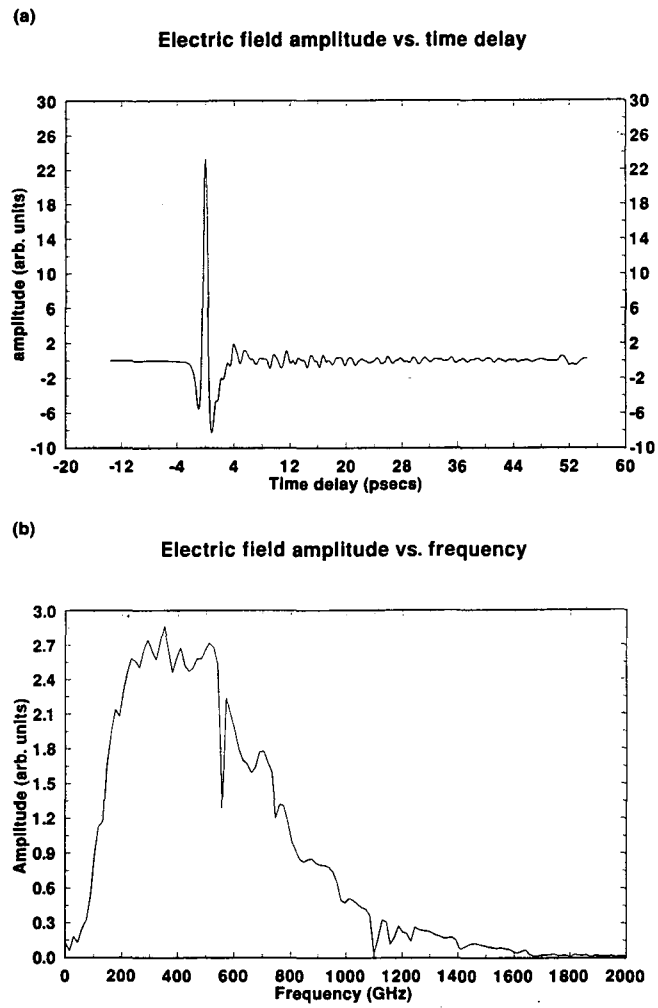

Fig. 2a,b. The temporal profile and Fourier transform of an electrical pulse produced in our laboratory are shown. The picosecond timescale pulse contains useful frequency components beyond 1 THz. The oscillatory structure which follows the peak of the pulse and the corresponding sharp dips in the spectrum are due to atmospheric water vapor. The average power in the beam is in the nanowatt range, corresponding to an electric field at the detector of approximately 1V/cm. The ratio of the peak amplitude to the off-peak noise is greater than 4000:1.

most important advances in these component systems are briefly discussed.

The generation and detection of the electrical pulse requires a source of subpicosecond optical pulses. A colliding-pulse mode-locked dye laser has been assembled for this purpose. It is now performing according to specifications, producing a train of 120 fs pulses with average power 25 mW. In addition, a continuous-wave (CW) Ti:Al_2O_3laser will be

adapted for mode-locked operation. To date the laser is operating in a CW mode and the necessary optics for mode-locking have been designed and acquired.

Antenna chips have been fabricated using both silicon-on-sapphire substrates with Al metallization and GaAs substrates with AuNiGe metallization. All of the processing is performed by the group using photolithography facilities on the UC Berkeley campus and e-beam evaporation in Bldg. 2 of LBL.

The free-space terahertz spectrometer is based on a system of off-axis parabolic mirrors to focus the beam onto both the sample and antenna. Mounts were designed and fabricated for the mirrors. The next entire optical system has been assembled and aligned using an incandescent point source. The next step will be placing the antenna and detector assemblies at two of the foci of the optical system to test the propagation of the terahertz beam through the entire optical system. In addition, an enclosure has been designed for the spectrometer that can be purged with dry nitrogen. This will eliminate potentially confusing contributions from water vapor absorption.

Raman Studies of Materials and High Temperature Systems

Principal Investigator: Gerd M. Rosenblatt

Funding: $213,900 (FY 91)
$252,800 (FY 90)

Project Description

Materials with useful mechanical and physical properties are often produced or processed at high temperatures and then utilized as components of composites, mixed phases, or films. The properties of the resulting engineering materials often depend crucially upon the ways in which the properties of the components are modified by processing and by their incorporation into the engineering material. For example, the mechanical properties of films depend upon the processing conditions and the substrate, and those of ceramics depend upon grain size and porosity, as well as composition and phase. Detailed understanding and optimization of the behavior of complex materials benefits from nondestructive in-situ measurements of strain and of associated changes in atomic and lattice vibrations of the individual components. Measurements on composite systems require spatial resolution and sensitivity reflecting the size of the individual components. Specialized Raman spectroscopic techniques have been developed to address these needs.

Raman spectroscopy (inelastic light scattering) probes the molecular and lattice vibrations of materials, can attain near-diffraction-limited spatial resolution, and can be configured for adequate sensitivity for many problems. The Raman effect is sensitive to strain in crystalline materials because Raman frequency shifts directly measure atomic lattice vibrations. A unique high-sensitivity imaging Raman instrument was used with near diffraction-limited spatial resolution to investigate changes in atomic and lattice vibrations produced by strain or processing.

Accomplishments

High-sensitivity, imaging Raman spectroscopy techniques developed and used in this laboratory have been used to study a number of technologically important, high-temperature materials. In collaboration with P. Funkenbusch of the University of Rochester, the phase-transformed zone was mapped (see Figure 3) in the vicinity of the contact point (6 mm ×7 mm) in a 25-mm diameter quarter sphere of partially stabilized zirconia subjected to carefully controlled, steady-state loading. The map contains information about the size and extent (e.g., up to 100% transformation at the contact point from 0% in the base material) of the transformed zone not available with other techniques. The map is being used to determine the appropriate yield criterion for this material for use in powder compaction models.

In collaboration with researchers at LBL and SSRL, Raman spectroscopic investigations of diamond thin films have continued. A profile of the diamond Raman line frequency and width from a prototype, free standing, 200-μm thick, diamond window shows that the film is uniform and stress-free. In collaboration with J. Kortright of CXRO/MSD there was a study on the effect of temperature on the thin amorphous carbon layers used in x-ray mirrors. It was shown that annealing causes microstructural changes consistent with layer shrinkage observed by TEM.

Exploratory experiments on electronic materials have been initiated. In collaboration with D. Morris

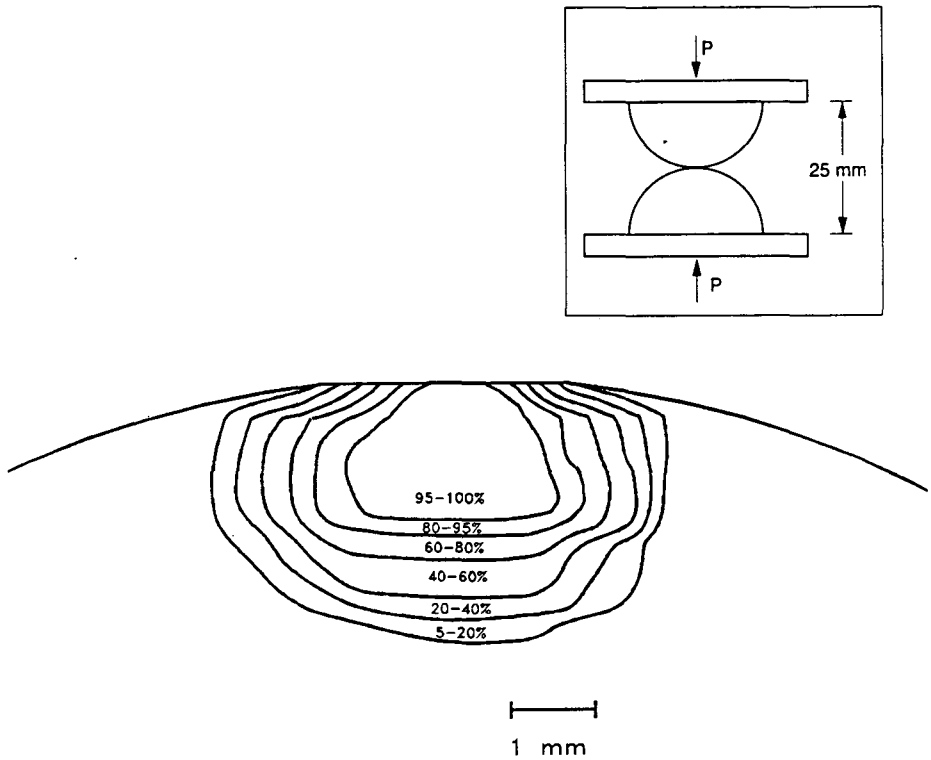

Fig. 3. Unique imaging Raman capability was used to map the phase-transformed zone (stable monoclinic zirconia resulting from transformation of the metastable tetragonal phase) produced when a quarter sphere of partially stabilized zirconia was subjected to carefully controlled, steady-state loading. The contour map comprises the analysis results of 2500 Raman spectra collected and analyzed in 2.5 hours using a unique spatially resolved Raman system and software. The measured contour rules out two of the three stress propagation models that have been developed to date for this system.

and J. Nickel of Morris Research, it was shown that oxygen isotope exchange in $YBa_2Cu_3O_7$ high-T_c superconductors is site specific, with the apical oxygen sites exchanging faster than the plane sites. In collaboration with E. Haller's group in MSD, local vibrational mode spectroscopy was used (utilizing the high sensitivity Raman system) to show (1) that the Be dopant impurities in low-temperature MBE-grown GaAs occupy substitutional (acceptor) sites, but are compensated by As anti-site defects in the as-grown material, and (2) that extended hydrogen platelet structures grown in crystalline Si are composed entirely of singly bonded Si-H structures with trigonal symmetry. In collaboration with V. Robbins of Hewlett-Packard, it was shown that band gap variations in prototype MOCVD-grown GaInP on GaAs LED's are due to compositional variations (most likely caused by reactor wall effects) by using a combination of imaging photoluminescence and profiling Raman spectroscopy.

Publications

Journals and Proceedings

D.E. Bliss, W. Walukiewicz, J.W. Ager III, E.E. Haller, K. Chan, and S. Tanigawa, "Annealing Characteristics of Low Temperature Grown GaAs:Be," *J. Appl. Phys.*, in press.

L.S. Pan, D.R. Kania, P. Pianetta, M. Landstrass, J.W. Ager III, S. Han, and O.L. Landen, "Carrier Mobility and Lifetime Measurements in Undoped CVD Diamond Films," *Science*, in press.

Other Publications

J.W. Ager III, D.K. Veirs, H.Q. Lee, and G.M. Rosenblatt, "Profiling and Mapping of Advanced Materials Using Spatially Resolved Raman Spectroscopy," in *Microbeam Analysis*, D.G. Howitt (San Francisco Press, 1991), pp. 105-108.

Femtosecond Dynamics in Condensed Matter

Principal Investigator: Charles V. Shank

Funding: $268,200 (FY 91)
$296,500 (FY 90)

Project Description

The purpose of this project is to develop a new short pulse laser source in the blue region of the spectrum with a pulsewidth in the femtosecond time domain. The laser will be a unique tool for the investigation of ultrafast processes in a class of molecules absorbing in the blue region of the spectrum.

In this project the plan is to apply newly developed laser instrument to the study of ultrafast processes in molecules. The first step in vision, the photoisomerization of rhodopsin, will be studied.

The newly developed source of femtosecond blue green optical pulses is ideal for the study of the isomerization of rhodopsin. The standard pump-probe technique was used in which a femtosecond pump pulse excites the rhodopsin sample, and the resulting changes in absorption are measured with a probe pulse, which is delayed with respect to the pump. The 35-fs pump pulses at 500 nm came directly from the amplifier. The 10-fs probe pulse was created by splitting off part of the pump and compressing it in an optical with a sequence of prisms for phase compensation. The 450 to 580 nm bandwidth of the probe permitted us to resolve the spectral dynamics of the rhodopsin molecule following excitation by the narrow band (~15 nm) pump pulses.

Accomplishments

The kinetics of the primary event in vision have been resolved for the first time. The 11-cis retinal prosethetic group of rhodopsin is excited with a 35-fs pump pulse at 500 nm, and the transient changes in absorption are measured between 450 and 580 nm with a 10-fs probe pulse. Within 200 fs, an increased absorption is observed between 540 and 580 nm, indicating the formation of the photoproduct on this timescale. These measurements demonstrate that the first step in vision, the 11-cis->11-trans torsional isomerization of the rhodopsin chromophore is essentially complete in only 200 fs. This indicates that the isomerization reaction is essentially barrierless.

Publications

Journals and Proceedings

R.W. Schoenlein, L.A. Peteanu, R.A. Mathies, and C.V. Shank, "The First Step in Vision: Femtosecond Isomerization of Rhodopsin," *Science* (in press).

Stimulated Desorption of Halogens

Principal Investigator: Jory A. Yarmoff

Funding: $42,200 (FY 91)
$31,100 (FY 90)

Project Description

Photon stimulated desorption (PSD) and electron stimulated desorption (ESD) are not only useful techniques for the determination of the local electronic and geometric structures of adsorbates on surfaces, but are also of fundamental and technological importance. Collectively, these processes are known as desorption induced by electronic transitions, or DIET. DIET is of fundamental importance in the area of radiation damage of surfaces, as well as in technological applications such as photolithography. Our program goals are aimed at both providing a better understanding of the mechanisms involved in DIET, and in employing DIET as a diagnostic for investigating halogen bonding on semiconductor surfaces.

The adsorption of halogens and halogen-containing species on semiconductor surfaces is being investigated as part of an effort to model the basic mechanisms involved in the plasma-assisted processing of semiconductors. The basic chemical interaction between simple atomic, molecular, and radical precursors with clean semiconductor surfaces is studied under ultrahigh vacuum conditions. In this way, the interactions of the important species present in the complicated plasma reactor environment can be understood on a fundamental level. The long-term goal is to provide a sufficient understanding of halogen surface chemistry so that new processes for etching and growth can be developed without a lengthy trial and error procedure.

The project is composed of both work carried out at synchrotron light sources and at the University of California, Riverside (UCR). At the light sources, soft x-ray photoemission spectroscopy (SXPS) and PSD are employed, while at UCR the techniques utilized are Low Energy Electron Diffraction (LEED), Auger Electron Spectroscopy (AES), Thermal Desorption Spectroscopy (TDS), and ESD. In general, techniques such as SXPS or AES are needed in order to characterize the surface condition prior to performing a DIET experiment. The DIET measurements involve measurements of the ion kinetic energies and ion yields as a function of the incident photon or electron energy. During this time the ESD apparatus was under construction; the data discussed below were collected at both the National Synchrotron Light Source at Brookhaven National Laboratory or at MAXLAB in Lund, Sweden.

Accomplishments

In previous work, it was shown that the PSD of F^+ from a silicon surface is a chemically selective process, i.e., the thresholds for PSD observed at the substrate core level edge coincide with the oxidation state of the bonding surface atom. Work continued with the fluorine-silicon system, in order to answer some important questions that remained, and have extended the work to other halogen-semiconductor systems, e.g., XeF_2/GaAs and Cl_2/GaAs.

In the XeF_2 etching of silicon, the observed gas-phase reaction product is primarily SiF_4, and an approximately 15-Å-thick reaction layer composed of a mixture of SiF, SiF_2, SiF_3, and SiF_4 intermediate species forms on the surface after etching. SXPS results, which probe the composition of the entire reaction layer, were compared with PSD data, which probe only the outermost component, as a function of fluorine exposure. This comparison showed that the surface of the reaction layer is terminated by SiF_3 after the steady-state reaction regime has been reached. Combining this result with work function and Fermi level position measurements, a model was developed for the fluorine etching of silicon. The model suggests that F atoms in the vicinity of the surface pick up an electron, forming a negative ion. The negative ion then reacts with holes in the valence band in order to form a bond to silicon. This model is in agreement with measurements of etch rate vs. exposure and doping level.

Of particular interest in the etching of III–V semiconductor materials is the interaction of Cl_2 with GaAs, since chlorine is the primary etchant employed in GaAs device fabrication. The surface chemistry during the room temperature adsorption on and etching of GaAs with Cl_2 was investigated. Not only are both As-Cl and Ga-Cl bonds observed, but a rich variety of higher chloride formation, e.g. $AsCl_2$ and $GaCl_2$, is seen as well. These species are the reaction intermediates involved in the etching process. At the highest exposures studied, a large buildup of $GaCl_2$ is observed, which may serve to inhibit further etching of the GaAs material. The conversion of $GaCl_2$ to the volatile Ga chloride species, $GaCl_3$, is thus the rate limiting step in the etching reaction at room temperature.

Although fluorine does not etch GaAs because of the nonvolatility of Ga fluorides, the reaction between F and GaAs is of importance to processes that involve growth via fluorinated precursor molecules. In addition, since the F^+ PSD signal is considerably larger than the Cl^+ signal, we have begun our GaAs PSD studies with this system. GaAs surfaces were exposed to XeF_2 and subsequently examined with SXPS and PSD. The PSD spectra have an incredibly large number of spectral features, as shown in Figure 4. At the present, we are analyzing these data in order to map out the spectroscopy.

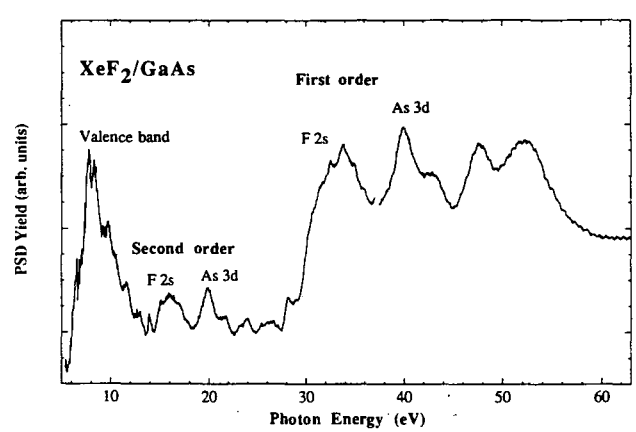

Fig. 4. Photon stimulated desorption of F^+ from a GaAs surface after reaction with XeF_2. The ion yield is shown as a function of the photon energy. Features due to adsorption of first and second order light are observed. The initial states corresponding each region of the spectrum are marked. The break at ~37 eV is due to a grating change.

Publications

Journals and Proceedings

J.A. Yarmoff, D.K. Shuh, T.D. Durbin, C.W. Lo, D.A. Lapiano-Smith, F.R. McFeely and F.J. Himpsel, "Atomic Layer Epitaxy of Silicon by Dichlorosilane Studied with Core Level Spectroscopy," *J. Vac. Sci. Technol. A*, in press.

S.A. Joyce, C. Clark, V. Chakarian, D.K. Shuh, J.A. Yarmoff, T.E. Madey, P. Nordlander, B. Maschoff and H.-S. Tao, "The Influence of Coadsorbed Potassium on the Electron Stimulated Desorption of Fluorine from PF_3 on Ru (0001)," *Phys. Rev. B*, in press.

D.K. Shuh, J.A. Yarmoff, A. Santoni, L.J. Terminello and F.R. McFeely, "Chlorine Chemisorption and the Onset of Etching on GaAs(110) at Room Temperature," Surf. Sci., in preparation.

S.A. Joyce, A.L. Johnson, J.A. Yarmoff and T.E. Madey, "The Structure and Chemistry of PF_3 Adsorbed on Ru(0001) as Studied by Electron Stimulated Desorption," *Surf. Sci.*, in preparation.

V. Chakarian, D.K. Shuh, J.A. Yarmoff, B. Maschoff, H.-S. Tao and T.E. Madey, "Coadsorption of PF_3 and Potassium on Ru(0001) Studied by High-Resolution Photoelectron Spectroscopy," *J. Chem. Phys.*, in preparation.

C.W. Lo, D.K. Shuh and J.A. Yarmoff, "The Geometric and Electronic Structure of the XeF_2/Si(111) Etching Reaction Layer," *Phys. Rev. B*, in preparation.

D.K. Shuh, and J.A. Yarmoff, "Chlorine Adsorption and Etching of Room Temperature GaAs(110) Studied by Soft X-ray Synchrotron Photoelectron Spectroscopy," *Appl. Phys. Lett.*, in preparation.

J.A. Yarmoff, D.K. Shuh, C.W. Lo, V. Chakarian and T.D. Durbin, "Photon Stimulated Desorption of Fluorine from Semiconductor Surfaces," in preparation.

C.W. Lo, D.K. Shuh and J.A. Yarmoff, "The Etching Reaction of XeF_2 with Si(111) at Elevated Temperature," in preparation.

Nuclear Science Division

Prototype Tracking and Timing Detectors for RHIC

Principal Investigator: Charles R. Gruhn

Funding: $102,300

Project Description

This project is to investigate the limits of time resolution attainable with a gas-based detector system. The effort is aimed at developing detector concepts optimized for use at new high multiplicity detectors, such as the Relativistic Heavy Ion Collider (RHIC). The goal is to develop a gas detector capable of better than 100-ps (σ_{rms}) time resolution in detecting minimum ionizing particles. In this first phase of the project the dependence of efficiency and time resolution on electrode design, electric field, and gas pressure was investigated. It was found that the temporal response of a high pressure Ar-CH_4 gas mixture yields rise times of less than 40 ps/mV, comparable to the best photomultipliers, for signals in excess of 50 mV without further amplification. This is sufficient to suggest a gas detector will meet the timing needs. Results were summarized in the presentation at the 1992 Vienna Wire Chamber Conference.

Accomplishments

First a high pressure gas detector research area was set up and instrumented for data acquisition. Then the temporal characteristics of the signals coming from a Multi-Wire Proportional Chamber (MWPC) as well as from a parallel plate avalanche chamber were studied. The experimental setup consisted of first an MWPC (20-μm wires, 2-mm pitch) and later a simple 1-cm^2 parallel plate detector, both of which are mounted inside a high pressure (tested to 200 atm) gas cell. Anodes were read into the 50-Ω input of a Tektronix Communication Sampling Analyser 803 oscilloscope. The oscilloscope was self-triggered and recorded the current signal waveforms produced at different operational parameters (field, pressure, concentration of Freon in the gas mixture) by electrons from a ^{90}Sr source within the gas cell. CAMAC ADCs and TDCs were also used to record amplitude and time spectra from the gas anode triggered by the signal from a small scintillator.

The first task was to show that by raising the gas pressure, p, the dispersion in the point at which the cascade initiating electrons were generated could be minimized. The dispersion is controlled by the first Townsend coefficient, α. A region in α previously unexplored, was investigated at pressures in excess of 15 atm. In the first series of tests it was shown that gains exceeding 10^7 are possible and inherently stable at pressures from 20-40 atm. It was noted that in the analysis of pulse height versus $E/\sqrt{p}$, discontinuous jumps occur at set values of $E/\sqrt{p}$ for different pressures, which indicate the onset of perhaps a new multiplication method. This phenomenon is not yet understood.

The second task was to show that the time structure of the pulses generated was conducive to high-precision timing measurements: namely, that the rise times were short and stable over periods associated with discriminator threshold crossings. The risetimes of the averaged waveforms normalized to their mean pulseheight show a common dependence on the quantity $HV/\sqrt{p}$, where HV is the applied voltage and p is the gas pressure. The fastest risetime per amplitude was obtained at a pressure of 22 atm. The data point corresponds to a risetime of 1.35 ns. Note that this figure has a significant contribution from electrons that drift a long distance in the gas. To achieve even faster risetimes the effective drift distance was reduced to a few 100-μm with the addition of a small fraction of Freon 13B1 (<2%) to the gas. The resulting risetime over amplitude shows risetimes as fast as 4.6 ps/mV at 18.4 atm.

The final proof that the concept can yield high-resolution time-of-flight requires timing the passage of charged particles with the gas detector as one component of a time-of-flight system. It was originally thought that this would be a simple task using a beta source and a set of trigger counters. However, the low energy of the emitted betas using very thin scintillators which lead to significant, path length dispersion from multiple scattering of the low energy electrons. The concept will be finalized with a test in a high energy particle beam in the near future.

Physics Division

Silicon Tracking System R&D

Principal Investigator: Murdock Gilchriese

Funding: $101,200

Project Description

This project initiated an R&D effort to explore very large silicon detector tracking systems for particle tracking in future collider experiments at hadron colliders.

The potential new generation of silicon vertex detectors requires combined design and analysis of mechanical, thermal, and electrical properties of the detector, supports, cooling, electronics, and cabling. A combined approach is needed to meet the requirements of few-micron spatial resolution, high-packing density, and low-mass structures, including on-board readout.

Accomplishments

Many variations of silicon detector module design were conceived. Early versions had the heat-producing readout electronics attached to the detector directly over an evaporative-cooled support ring surface. Later versions moved the electronics relative to the cooling/support ring to decrease both the detector temperature and deflection due to thermal gradients. Each one of these designs was analyzed using ANSYS. The studies concentrated on reducing the detector temperature to a low level so that the contribution of shot electrons to noise would be acceptable and the deflections due to thermal gradients would be low.

The result of the studies indicated that the selected baseline design has < 2 μm deflection at the detector end due to thermal gradients. Other contributions to the total deflection were gravity (50 μm) and the effect of cooling from room temperature to the 0°C operating value (10 μm). The conclusion of the studies demonstrates the feasibility of providing the required spatial resolution under mechanical and thermal loads. Studies of low-max cabling techniques were also initiated and preliminary results indicate the feasibility of developing suitable aluminum on kapton cabling.

The detector centerline temperature along the length was determined, and the increase in shot noise charge was estimated. It was assumed that the detector bias current increased exponentially by a factor of 2.5 for a 10°C temperature rise. In addition, the initial number of shot electrons at a detector temperature of 0°C was assumed to be that at the end of 10 years of irradiation.

The increase in detector bias current for the worst case considered was 108%. Since the total noise is composed of charges due to current in the detector, the biasing resistor and the preamp and the noise charge is proportional to the square root of the bias current, the percent change in the total noise charge was only 6.0%. This implies that the signal-to-noise ratio will not drop by more than 10% due to the maximum expected temperature increase of the detector. Further system-level studies are required to validate all aspects of the mechanical, thermal, and electrical properties by fabrication of a prototype.

Data Acquisition Electronics R&D

Principal Investigator: Michael Levi

Funding: $107,000

Project Description

Effort to extend the state-of-the-art high bandwidth data-acquisition systems that are essential to the successful operation of particle physics detectors is envisioned in future high-luminosity experiments.

Accomplishments

The work on DAQ protocols and techniques has been focused on high-luminosity collider R&D. A complete DAQ scenario readout has been formulated and as well as participation in discussions and formulation of a draft DAQ protocol.

Included in this is a formulation for control of the readout, error handling, calibration, debugging environments, and high speed interfacing to the front-ends. The design model uses a "push" type architecture where data transmission is under the control of the sender. By command of the DAQ

system, data are "packetized" by the front-ends and then transmitted along with control headers to a buffer receiver. The buffers serve to de-randomize the data rates prior to eventual transmission into the event switch and onto the processor farm. The buffers can store many large data packets, up to two hundred before retransmission. The buffers also serve the dual purpose of local debugging and control. Packets can be spied on and locally processed. Calibration and hardware debugging can be performed by this feature. This concept is called a "local area node" and has been implemented in the OPAL DAQ.

Data are retransmitted in high speed optical links from these buffer nodes to the event switch. The event builder is very likely to be a combination of multiplexors, which funnel or increase the data rate on an individual link and a high speed switch. Data will flow off an high luminosity detector at an average rate of one to ten Gbytes/sec in a thousand optical links. Present day optical data links can only sustain 30–125 Mbytes/sec. The data are first combined into a smaller number of high speed links before passing through an event switch. Commercially available data switches have been evaluated. Data would pass through these switches and directly into the processor farm crates. Within each crate an additional level of demultiplexing would distribute the data to the destination processor. Such a system, based on components that have come available this year could become backbone of a data-acquisition system such as a solenoidal detector for the SSC, the STAR detector for relativistic heavy ion collider, and for the CDF detector at Fermilab. It is intended to construct a prototype switch in conjunction with a set of optical links.

The third area of work has been directed toward assembling a cost effective fiber-optic data link. The telecommunications industry requires data to be transmitted over great distances, and the cost reflects the use of very high-power long wavelength lasers (1310 nm) and very sensitive photo-detectors (avalanche photo-diodes) and low noise GHz preamplifiers. These high power lasers tend to be unreliable and fail in 50000 hours. The data are transmitted on single-mode fibers (6–9 micron diameter). Under the ERF project we have pursued a different approach. For short haul data communications (<1 km) multi-mode fibers can be used (50 micron diameter). These fibers transmit 100 times more light than the single mode fibers, which eases the requirements for both transmitter and receiver. The multi-mode fibers may be used over these short distances because of the advanced design of these fibers. Typically, multi-mode fibers can transmit data at 1 Gbit/sec over 1 km. For shorter distances the rates are proportionally greater. Additionally, low-power short wavelength lasers (780 nm) such as the type that are used in compact disk players are well matched to one of the optimal transmission windows of these fibers. These solid-state lasers typically cost $1.25 each and have 1 million hour reliability. The combined use of a short wave laser and a multi-mode fiber is not suitable for telecommunications purpose but is well suited to data communications.

Research Medicine and Radiation Biophysics Division

ALS Life Sciences Initiative

Principal Investigators: Thomas F. Budinger and David T. Attwood

Funding: $75,000

Project Description

The combination of life sciences research talent, expertise in x-ray optical techniques, and high brightness, partially coherent x-ray emissions at the ALS will give LBL unique opportunities for first-in-the-world scientific breakthroughs. To realize those opportunities in a timely fashion new efforts must be accelerated and focused. The major purpose of this proposal is to perform the conceptual studies for the beamlines and experimental stations to enable the exploration of this new field.

A well-structured and well-directed effort is required to pull together the Laboratory's strengths. Life science programs must be clearly articulated and available in both written documents and presentation material. The connection to light source brightness and coherence must be clarified, as well as the relationship to capabilities (uniqueness and compatibility) at other facilities. This involves a concerted effort on the part of a physicist or engineer technically competent in ALS technologies. Long lead-time technical issues need to be coupled to end-station requirements and sample preparation issues. Preliminary layouts must be agreed upon, special issues identified and resolved, and a critical path to early implementation laid out in detail.

It has been decided to organize these efforts within RMRB and CXRO, with the participation of a scientific council drawing on individual strengths from several LBL divisions. The effort permits organization of governmental, industrial, and university proponency activities in a concerted effort to undertake critical pre-construction design studies. Support is needed in the effort to formulate successful strategies, alternate plans, and community interactions that will help to accomplish these ends.

Accomplishments

This project has contributed to the formulation and coordination of potential new projects from the three Life Sciences Divisions at LBL and in particular has helped in developing projects within RMRB and CXRO for the application of synchrotron microscopy to the analysis of micro deposits of calcium in heart and brain tissue. Additional key projects came from LBL's Applied Science Division. Contributions were also made in reviewing the LBL publications in Structural Biology and participation in the Structural Biology Program planning meetings. The current organization plan for x-ray microscopy at the ALS has been developed.

Viability in Synchrotron Microscopy

Principal Investigator: Thomas L. Hayes

Funding: $32,000 (FY 91)
$77,400 (FY 90)

Project Description

New synchrotron radiation sources will provide soft x-ray radiation that can be directed to a very small area of the biological specimen. The relative transparency of water as compared to carbon and nitrogen over a large part of the soft x-ray region will permit hydrated specimens to be studied and the reduction in possible artifacts both in structure and elemental distribution should be significant. Viability can be a useful criterion for determining the degree of artifactual changes taking place in a biological sample during preparative and analytical steps. Cryofixation followed by low temperature analysis has been shown to be a valuable technique in reducing artifacts of specimen preparation and will play an important part in studies of the preparation of "living" biological samples for analysis at next generation proton sources. This study attempts to evaluate the possibility for viable biological specimens to be examined by soft x-ray microscopy with particular attention to the viability of frozen-hydrated material following microscopy in

whole cell mounts or just prior to cryosectioning for frozen-hydrated tissue section mounts.

Although there has been considerable progress towards the cryopreparation of viable individual cells in the past twenty-five years, there has been relatively little advancement in low temperature viability protocols for the preparation of more complex tissue. Basic information is needed on the effects of freezing and thawing in multi-cellular systems and on the effects of cryoprotectants. In particular, the ultrastructural morphology and elemental electrolyte chemistry at each stage of the slow freezing and thawing associated with maintaining viability can be captured for analysis through the use of the very rapid snap freezing techniques that have been developed for the analysis of non-viable biological material. The possibility for dynamic studies using the focused beam at facilities such as the ALS can be better assessed if more information is available on the viability of biological tissue under the severe radiation and temperature stress associated with the preparation and examination of biological specimens. This project will provide preliminary measurement of certain of the radiation sensitivity and cryofixation parameters and enable a more accurate evaluation of proximity to the ultimate goal of high resolution examination of living tissue.

Two specimens of plant material resistant to low temperature were used in this study. A specialized form of the leaf of the aquatic plant Lemna (Duckweed) will be utilized to test the survival of multi-cellular tissue following soft x-ray irradiation under conditions simulating those that will be used for scanning x-ray microscopy at synchrotrons. A second group of tissues from apple twigs will be used to evaluate the presence of ice in the extracellular spaces and the ability of the cells to tolerate the accompanying stresses of dehydration.

Accomplishments

Experiments with viable plant material in the low temperature scanning electron microscope system have shown that plant cells in complex tissues can survive the environmental conditions associated with the proposed ALS scanning x-ray microscope. In particular the initial question of water movement during cryofixation was studied. Although such water movement has been considered to be critical to plant survival under extreme low temperature conditions (see "Life in the Cold," P.J. Marchand, Univ. Press of New England, 1987) the structural biology of water movement at the cellular level and below has not been well understood.

Models of water movement using the liquid lining layers of the lung were developed and tested on the low temperature scanning electron microscope. Quantitative assessment of the geometry of the cryofixed specimens were carried out utilizing new advances in microscope probe pattern and display system to connect for any distortion and calibration measurements to evaluate tilt angle accuracy and hysteresis.

While in some special circumstances measurements from a single micrograph can accurately represent the dimensions of the specimen, three dimensional data generally requires the measurement of stereo pair images. The information gained in these experiments will help to identify the most efficient methods for evaluating the cryofixed specimens' dimensions as they are examined in the ALS microscope stage system.

Publications

Journals and Proceedings

J. Bastacky, T. Hayes, D. Yager, and C. Lee, "Quantitative Geometric Scanning Electron Microscopy," in *Proceedings of the 49th Ann. Meeting of the Electron Microscopy Society of America*, San Francisco Press, Inc. (1991).

Scintillation Mechanisms of Heavy Atom Scintillators

Principal Investigators: William W. Moses and Stephen E. Derenzo

Funding: $49,700 (FY 91)
$60,500 (FY 90)

Project Description

The purpose of this project was to study the scintillation mechanisms of heavy-atom inorganic scintillators using a vacuum ultraviolet (VUV) synchrotron light source. The ultimate goal of this research is to develop denser, faster, and more luminous scintillators for *medical imaging* and *nuclear radiation detection* instrumentation. Ultraviolet

photoelectron emission spectroscopy was used (UPS) to identify the electron energy levels, and fluorescence emission spectroscopy (FES) was used to identify the energy level transitions that cause the scintillation. The synchrotron beamline monochromator and a commercial cylindrical mirror electron energy analyzer were used to perform the UPS measurements, and the beamline monochromator and a commercial analyzing monochromator and photomultiplier tube were used to perform the FES measurements.

The positions of the outermost molecular energy levels (typically 5 eV to 25 eV) were measured in order to predict scintillation via a mechanism known as the crossover transition. Compounds that satisfy the energy inequality $\Delta E_2 < \Delta E_1$, where ΔE_1 refers to the energy difference between the valence band and the conduction band and ΔE_2 refers to the energy difference between the outermost core band and the valence band, should fluoresce via a crossover transition and thus be fast scintillators. However, measurements of the molecular energy levels of inorganic heavy atom compounds are only available for a few compounds, so these energy levels were measured for known and candidate scintillating compounds using ultraviolet photoelectron emission spectroscopy (UPS). Monochromatic ultraviolet photons from a synchrotron vacuum ultraviolet (VUV) source impinge upon the scintillator, liberating photoelectrons whose kinetic energy is measured with a commercial cylindrical mirror analyzer (Figure 1). Each photoelectron has a kinetic energy equal to the (constant) energy of the incident photon minus the electron's binding energy, so measuring the photoelectron kinetic energy is equivalent to measuring the energy of the molecular level that the photoelectron came from. The electron population density is then determined by measuring the energies of all liberated photoelectrons.

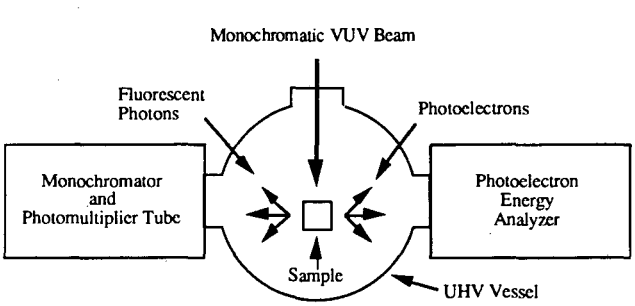

Figure 1: Diagram of the Experimental Apparatus

Fig. 1: Diagram of the experimental apparatus.

Once the energies of the populated molecular energy levels are known, the levels that participate in the fluorescent decay were determined using fluorescence emission spectroscopy (FES). The emission wavelength spectrum of the scintillator was measured by exciting the compound with high energy (>50 eV) photons from the VUV source and analyzing the wavelength of its fluorescent emissions with a monochromator and a photomultiplier tube. The analyzing monochromator was then set at the peak of the emission spectrum and the energy of the VUV beam scanned. When scintillation intensity is plotted as a function of VUV beam energy, the location of thresholds helps identify participating energy levels. For example, the fast scintillation in BaF_2 is caused by a transition from the $2pF^-$ band to the $5pBa^{2+}$ band. Therefore, the scintillation light output is low when the VUV beam energy is less than 18.3 eV (the energy of the $5pBa^{2+}$ band) and becomes much higher when the VUV beam energy is greater than the 18.3 eV threshold.

Accomplishments

During this fiscal year there have been two three-week experimental runs at the Synchrotron Radiation Center in Madison, WI, during which time UPS measurements of 21 compounds and FES measurements of 15 compounds were made. It is now believed that the scintillation mechanism of CeF_3, which is slightly more complicated than the ultra-fast mechanism described above, is understood and a publication that describes the mechanism is being prepared. This understanding has led to postulation that the scintillation properties of CeF_3 could be enhanced by doping it with LaF_3, effectively "designing" a new scintillator. Further tests confirmed this theory, and these results have been published and patented.

Results obtained from these studies have been used to guide, by suggesting promising stoichiometric compounds and host crystal/dopant combinations, a separately funded scintillator search, which is described in a publication recently submitted for publication. In addition, the scintillation properties of the two most promising compounds found by this search (lead carbonate and lead sulfate) have been described in separate publications, and the scintillation properties of one of these materials (lead carbonate) patented.

The UPS and FES techniques described above have been improved for use with scintillator crystals.

Scintillator crystals tend to have high surface resistivity, and so accumulate an electrical charge when exposed to the VUV beam. This charge (and local variations in this charge) alters the photoelectron kinetic energy spectrum, and so gives an inaccurate measurement of the electron population density. Several schemes to both neutralize and minimize the variations in this surface charge and so obtain more accurate measurements of the electron population density have been developed.

Publications

Journals and Proceedings

W.W. Moses and S.E. Derenzo, "The Scintillation Properties of Cerium-Doped Lanthanum Fluoride," *Nucl. Instrm. Meth. A299*, 51 (1991).

W.W. Moses, S.E. Derenzo, P.J. Levy, and J.A. Kierstead, "Further Measurements of the Scintillation Properties of Lead Carbonate," *IEEE Trans. Nucl. Sci., NS-38*, 648 (1991).

W.W. Moses, S. E. Derenzo, and P. J. Shlichta, "Scintillation Properties of Lead Sulfate," submitted to *IEEE Trans. Nucl. Sci.* (LBL-31456).

S.E. Derenzo, W.W. Moses, J.L. Cahoon, T.A. DeVol, and L. Boatner, "X-ray Fluorescence Measurements of 412 Inorganic Compounds," submitted to *IEEE Trans. Nucl. Sci.* (LBL-31458).

Acronyms and Abbreviations

AES	Auger Electron Spectroscopy
AFM	Atomic Force Microscopy
ALS	Advanced Light Source
CXRO	Center for X-Ray Optics
DIET	desorption induced by electronic transitions
DOE	U.S. Department of Energy
EREM	Extended Resolution Electron Microscopy
ERF	exploratory R&D fund
ESD	electron stimulated desorption
FELs	free-electron lasers
FES	fluorescence emission spectroscopy
HMEC	human mammary epithelial cells
IR	infrared
LBL	Lawrence Berkeley Laboratory
LEED	Low Energy Electron Diffraction
MWPC	Multi-Wire Proportional Chamber
PBPK	physiologically-based pharmacokinetic
PEL	permissible exposure limit
PSD	photon stimulated desorption
RHIC	Relativistic Heavy Ion Collider
RMRB	Research Medicine and Radiation Biophysics Division
STEL	short-term exposure limit
STM	Scanning Tunneling Microscopy
SXPS	soft x-ray photoemission spectroscopy
TDS	Thermal Desorption Spectroscopy
TEM	Transmission Electron Microscope
TOF	time of flight
UC	University of California (Berkeley)
UCR	University of California, Riverside
UPS	ultraviolet photoelectron emission spectroscopy
UV	ultraviolet
VUV	vacuum ultraviolet

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