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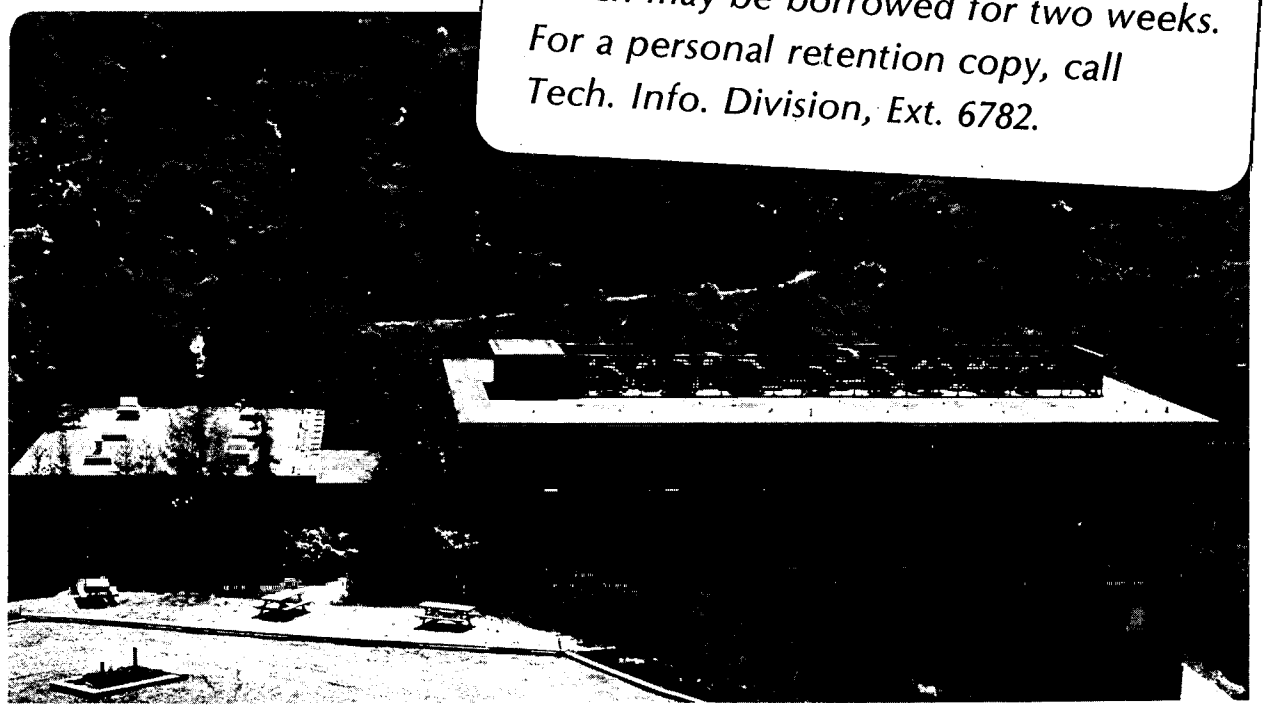

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ARPES Investigation of Intrinsic Surface States on the Ge (001) 2x1 Reconstructed Surface

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Abstract

Synchrotron radiation excited angle-resolved photoelectron spectra of the Ge (001) 2x1 reconstructed surface reveal two surface states 0.6 and 1.3 eV below the bulk valence band maximum at the gamma point of the surface Brillouin Zone. These two states are similar to those observed previously for Si (001) and GaAs (001) surfaces. The dispersion of the Ge bands with $k_{||}$ is qualitatively in agreement with the calculations of Chadi using his asymmetric dimer model for Si (001) 2x1.

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The 2x1 reconstructions of Ge (001) and Si (001) have been studied for years. The various structural models that have been proposed for these surfaces have been summarized by Chadi [1]. Recently, Jona and coworkers [2-4] compared LEED current-voltage plots calculated for many of these models to experimental data. They have shown that although none of these models are completely satisfactory, the best agreement is obtained using asymmetric dimer models similar to those determined by Chadi [1,5] for Si (001) using his energy minimization technique. In this paper, surface states observed by angle-resolved photoelectron spectroscopy (ARPES) studies of a Ge (001) 2x1 surface are shown to be in qualitative agreement with a band structure calculated by Chadi [1,5] for the asymmetric dimer model of Si (001) 2x1. There are also remarkable similarities in the ARPES spectra of Ge (001) 2x1 from this work, Si (001) 2x1 from Himpsel and Eastman [6], and GaAs (001) 4x2 Ga-stabilized surfaces from Larsen, et. al. [7] that suggest all three surfaces have similar geometries.

The Ge sample used in this study was prepared from a surface oriented to within 0.5 degrees of a (001) plane using Laue x-ray backscattering and polished using a goniometer similar to that described by Wendelken [8]. After using an Al_2O_3 polishing compound with 0.05 micron grit size and chemo-mechanically polishing with a 5% bromine in methanol solution, the sample was mounted in the vacuum chamber in which the base pressure was 3×10^{-10} torr. Studies previous to the UPS measurements showed that standard Argon ion bombardment and annealling (900 K) produced a strong 2x1 LEED pattern

with two perpendicular domains of equal intensity, while Auger spectra collected using the LEED apparatus in retarding field mode showed only a small residual carbon contamination on the sample. LEED and Auger measurements were not available during the actual UPS experiment.

The photoelectrons were collected using a 180 degree hemispherical analyzer with an acceptance cone half-angle of three degrees [9]. The photon source for the photoemission experiments was the eight degree port of Beam Line I at the Stanford Synchrotron Radiation Laboratory, which yielded useful photon fluxes between 9 and 29 eV. The total analyzer plus monochromator resolution was less than 0.2 eV. The experimental UPS spectra shown in FIGS. 1 and 2 were taken with a sample temperature of 170 K to minimize the thermal scattering contribution to indirect (phonon assisted) transitions in the spectra [10]. The differences between these spectra and those collected at room temperature were minimal.

Several normal emission spectra are presented in FIG 1. The valence band maximum (VBM) position was taken to be 7.69 eV above the second lowest L_6 valence band (which produced a prominent, dispersionless feature in several of the ARPES spectra) as determined theoretically by Chelikowsky and Cohen [11]. These calculations agree extremely well with the bulk features observed in ARPES spectra [12] and therefore were considered to be an excellent reference for determining the VBM position. Two spectra are shown for each photon energy; one for the clean Ge (001) 2x1 surface (solid line) and one

for the Ge sample after an 80 Langmuir exposure to oxygen. Each pair of spectra, at a given photon energy, have been normalized to the largest bulk feature. The attenuation in the low binding energy peaks that occurs upon oxygen exposure indicates that they may arise from surface states. Since the two features at 0.6 and 1.3 eV neither show any dispersion with photon energy for normal photoemission nor correspond to any flat band regions in the three dimensional band structure [11] of Ge, their identity as surface states is confirmed.

Low binding energy surface states on Ge (001) have been observed previously by Rowe in angle-integrated photoelectron spectra [13]. Similarly, two low binding energy surface states have been observed in normal emission ARPES spectra of Si (001) 2x1 at 13 eV photon energy by Himpsel and Eastman [6] and also several different GaAs (001) surfaces prepared using molecular beam epitaxy by Larsen et. al. [7]. In fact, normal emission spectra from the Si (001) 2x1 and the Ga-stabilized GaAs (001) surfaces can be found which are nearly identical to Ge (001) spectra.

The photon energy dependence of the surface states in FIG. 1 is especially interesting. At the lowest photon energies, the 0.6 eV peak is the more intense surface feature, but at higher photon energies the 1.3 eV peak is more intense. This behavior is similar to that observed in atomic photoemission from states with different angular momentum quantum numbers (l) [14]. For example, at low photon energies, p states have a higher photoemission cross section than s states,but the

p cross section decreases with increasing photon energy much faster than that for s states. Thus, the photon energy dependence of the surface states at gamma indicates that they have different symmetry properties, with the 0.6 eV peak having a higher l character than the 1.3 eV peak. Also, neither surface state is in a band gap of the Ge bulk band structure, so that they must be of different symmetry types than the Ge valence bands.

Varying the photoemission angle with respect to the surface allows the component of the wavevector parallel to the surface ($k_{\parallel}$) to be changed. In this fashion, the surface state $E(k_{\parallel})$ dispersion relation can be mapped. Several off-normal ARPES spectra were collected, some of which are shown in FIG. 2. These spectra clearly show that the surface states disperse with $k_{\parallel}$, but since there are 2x1 domains on the surface oriented perpendicular to one another, rotating in the plane which contains the [001] and [110] axes changes $k_{\parallel}$ simultaneously in two perpendicular directions (from gamma to J and from gamma to J' in the surface Brillouin Zone shown in FIG 3). Thus, it was not possible to assign an unambiguous experimental surface band structure from this data alone. Himpsel and Eastman [6] circumvented this problem by rotating their Si (001) 2x1 crystal in the plane containing the [001] and [010] axes, for which the two possible paths in the two dimensional Brillouin Zone are equivalent. No calculations of a surface band structure exist along this line, although it does include three points in common with Chadi's calculation [1,5].

The experimental data for $E(k_{\parallel})$ have been plotted in FIG. 3 with the gamma to J and gamma to J' directions in reciprocal space superimposed. The observed dispersion is consistant with the band structure calculated for the asymmetric dimer model [1,5]. However, it is also consistant with the surface band structure of Si(001) 2x1 determined by Himpsel and Eastman [6], which shows two surface states at J' instead of one. Further experimental results are required to elucidate this point, but at present it is not certain that a unique experimental band structure can be obtained along J'-gamma-J of the surface Brillouin Zone for the 2x1 reconstructed surfaces. One interesting point to note here is that the tight-binding parameters for Si used by Chadi in the surface band structure calculation actually yielded a Ge-like bulk band structure, with the lowest conduction band appearing at L rather than X for Si [15]. Thus, one might expect the calculations of references 1 and 5 to be more relevant to Ge than Si. For the GaAs study [7], the photoelectron analyzer acceptance angle was large compared to the dimensions of the two dimensional Brillouin Zone of the 4x2 reconstructed surface, so that the authors were not able to map the dispersion of the surface bands with $k_{\parallel}$.

In conclusion, ARPES spectra collected from a Ge (001) 2x1 surface have shown the existance of two low binding energy surface states. For normal emission spectra, the two Ge surface states are very similar in appearance to those observed on Si (001) and GaAs (001) surfaces. This observation implies that the geometry of all three surfaces is similar. Moreover, the $k_{\parallel}$ dispersion of the Ge surface states is consistant with

the two dimensional band structure calculated by Chadi for his asymmetric dimer model of Si (001) 2x1. Thus, this model may be reasonably close to the actual structure of the Si, Ge, and GaAs (001) surfaces.

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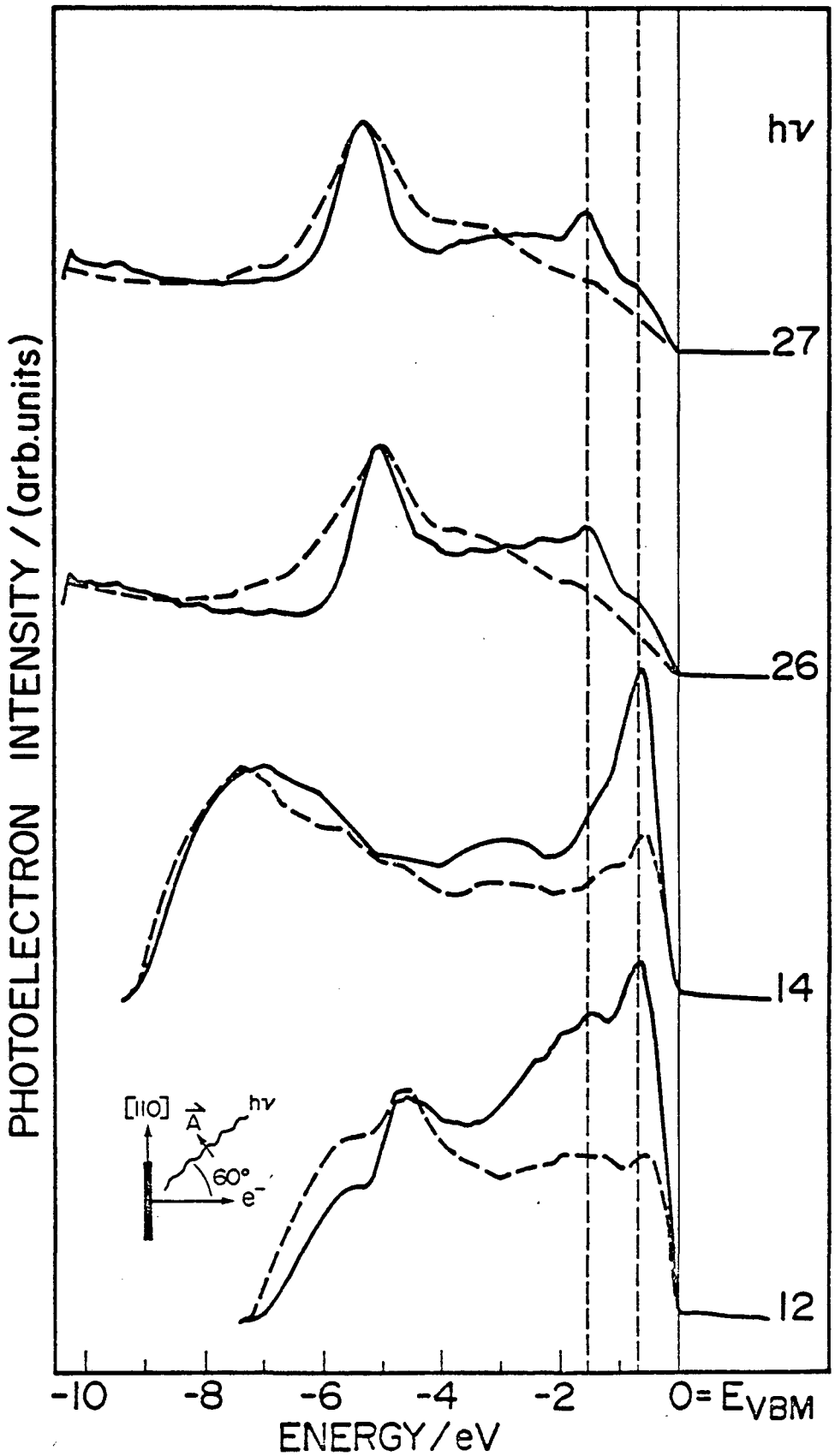
Figure Captions

FIG. 1 ARPES spectra of clean Ge (001) 2x1 (solid line) and Ge(001) after a 80 Langmuir exposure to oxygen (dashed line) taken at normal emission. The two vertical dashed lines show the positions of the surface states.

FIG. 2 ARPES spectra of Ge (001) 2x1 taken at various angles (Θ) for off-normal photoemission. The dispersion of the low binding energy surface states with $k_{\parallel}$ can be clearly seen.

FIG. 3 Experimental surface band structure of Ge (001) 2x1 which shows qualitative agreement with an asymmetric dimer model band structure calculation of Si (001) 2x1 [1,5]. The two perpendicular domains are shown at the top of the figure.


hν
27
26
14
12
PHOTOELECTRON INTENSITY / (arb.units)
[110]
A
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60°
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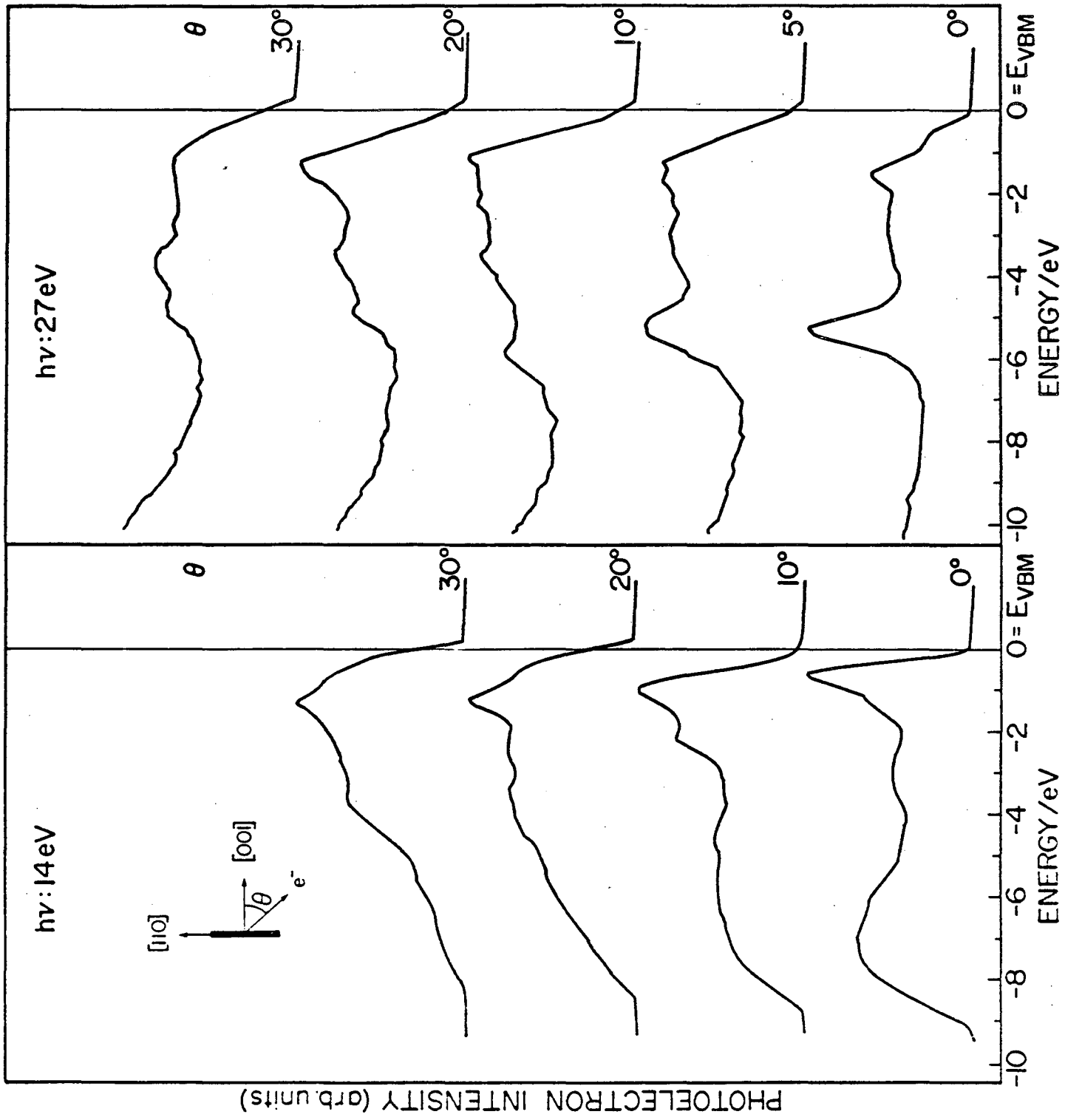
-10
-8
-6
-4
-2
0= E_VBM
ENERGY / eV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θ
30°
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ENERGY/eV
-10
-8
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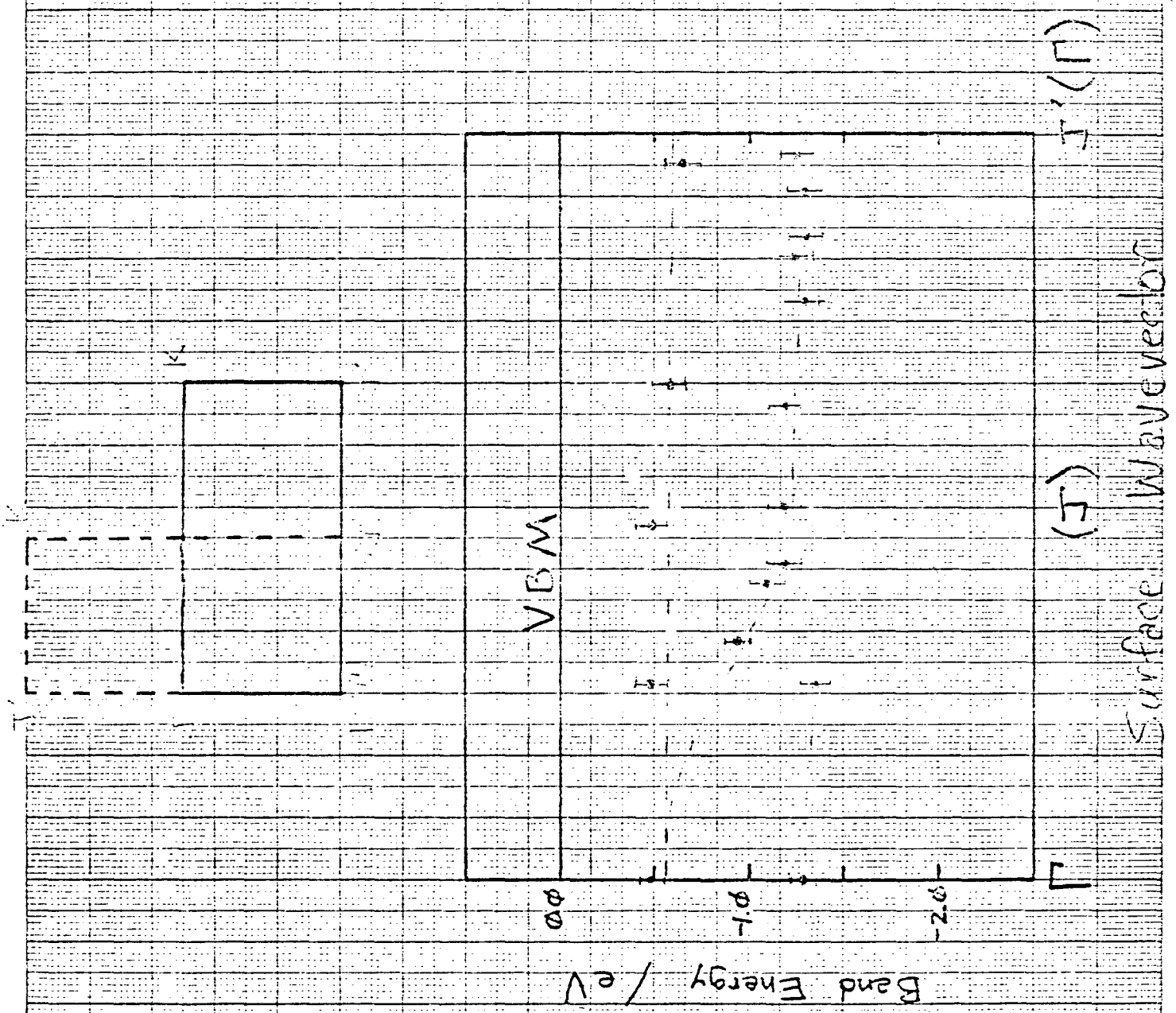
PHOTOELECTRON INTENSITY (arb.units)


VBM
Γ
(J)
J'(Γ)
Surface Wavevector
0.0
-1.0
-2.0
Band Energy / eV

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