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PRESSURE DEPENDENCE OF DEEP CENTERS BY CAPACITANCE SPECTROSCOPIES INSIDE THE DIAMOND ANVIL CELL

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Abstract: The use of diamond anvil high-pressure cells to study deep centers in semiconductors by means of capacitance transient spectroscopies is described. The technique is illustrated by recent results on DX centers induced by pressure in GaAs, the P_b center at the SiO_2/Si interface and the Schottky barrier formed by Pt on GaAs.

I. Introduction

Pressure can change the band structure of a semiconductor without changing its composition or symmetry.[1] Thus pressure is a powerful technique for studying the influence of band structure on the properties of defects in semiconductors. Pioneering work in this area has been carried out using conventional pressure vessels. These conventional pressure cells either cannot achieve very high pressure or do not have optical access to the sample. With the development of the diamond anvil cell (DAC) it is possible to achieve both high pressures and optical access to the sample.[2] Many shallow impurities and a few deep centers have been studied with the DAC using optical techniques.[3] Many defects, especially deep centers, are important in semiconductor technology because of their electrical characteristics. Thus it is desirable to develop methods for carrying out electrical measurement on samples inside the DAC. Furthermore such methods will make it possible to perform electro-optical measurements inside the DAC. In this article we will review the techniques for performing transient capacitance and photocapacitance measurements inside the DAC developed at Berkeley. The usefulness of these techniques will be illustrated by results obtained on a number of different deep centers in GaAs and Si.

II. Experimental Techniques

The major difficulty in making electrical measurements inside the DAC lies in making electrical contacts to the sample with wires. High pressure is achieved in a DAC by pressing two diamond anvils on a metal gasket. The sample and the pressure medium are confined in a hole drilled in the gasket. To make electrical contact to the sample inside the pressure medium, wires have to pass through the contact region between one of the diamond anvils and the gasket. Thus the wire has to be insulated from the metallic gasket. Unless the wires are protected in some way, they are also easily cut by the diamond anvil. Various methods have been devised to solve these two problems. To avoid shorting the wires through the gasket, insulating gaskets have been tried,[4] but most insulating materials do not yield like a metal so they are not satisfactory as gaskets. Another approach is to insulate the gasket from the wires by coating it with an insulator.[5,6] Typically a thin layer of Al_2O_3 is deposited on a metal gasket by plasma spraying or sputtering. The disadvantage of

this technique is that most laboratories may not have plasma spraying or sputtering facilities. The gaskets have to be indented and then sent away to be coated with Al_2O_3. As an alternative to the spraying or sputtering, Erskine et al.[7] applied Al_2O_3 in the form of fine powder (grain size about 1 micron or less). The powder is compacted into a layer of about 30 microns thick on the indented gasket using the diamond anvils. The disadvantage of this method is that the Al_2O_3 powder tends to spill over into the hole for the pressure medium. If Al_2O_3 powder fills the hole, the pressure generated is not hydrostatic. Erskine et al. alleviated this problem by adding a softer powder, such as $CaSO_4$, as the pressure medium inside the hole. A schematic diagram of the gasket, sample and wire after installation inside the cell is shown in Fig. 1.

Using ruby fluorescence the pressure distribution inside the powder have been found to have an inhomogeneity of about 10 % at pressures of about 300 kbar.

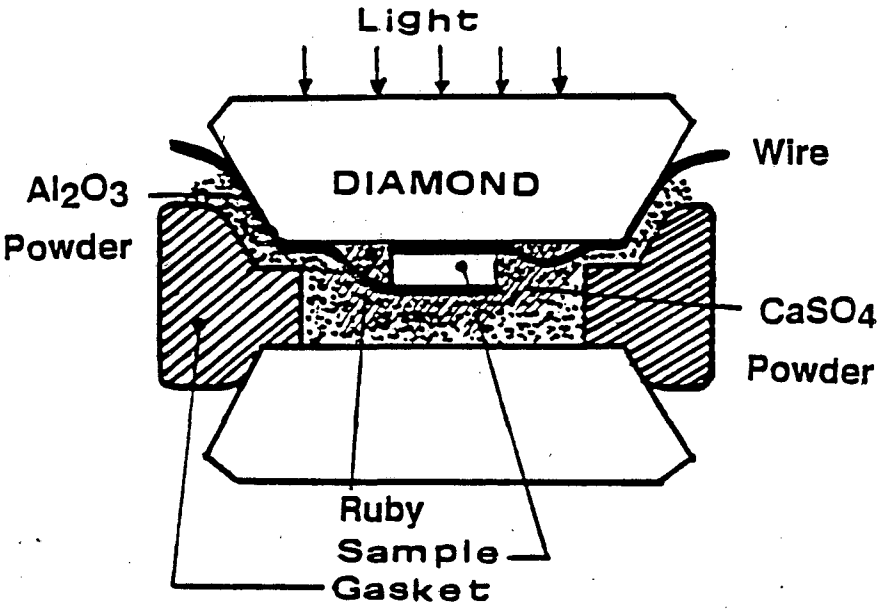

Fig. 1 Schematic diagram of sample attached to wires inside the DAC

Using this method of introducing wires into the DAC we have carried out capacitance measurements on diodes inside the DAC . Since the resistances of these diodes under reverse bias are very high, the pressure medium must be a good insulator. In this respect, powders of good insulators such as $CaSO_4$ has an advantage over liquid pressure media. However, diodes can also be destroyed by large pressure gradients. So far we have succeeded in making capacitance measurements on diodes at pressures up to about 40 kbar. In addition to capacitance, we have made transient measurements such as deep level transient spectroscopies[8] (DLTS) or constant capacitance voltage transient spectroscopy on samples inside the DAC. The advantage of such transient experiments is that a small change in the diode capacitance caused by changing the bias can be more easily detected on top of a large constant background stray capacitance. In DLTS measurements the sample temperature was monitored by a calibrated Si diode thermometer attached to the diamond anvil nearest to the sample. To minimize the temperature difference between the sample and the diode sensor, the cell temperature was changed very slowly (about 2 K/min or less). To achieve a short equilibration time between the sample and thermometer, the thermal mass of the cell should be minimal. This has been achieved by separating the lever system used to apply the pressure from the cylinders holding the anvils. Pressure is applied to the cell via a hydraulic press. Once the desired

pressure has been reached the pressure is maintained by a locking ring on the cell.[7] Since pressure less than 100 kbar is quite sufficient for defect studies, even smaller DAC can be used. The linewidth of DLTS spectra is inherently rather broad so the larger pressure inhomogeneity associated with a solid pressure medium is not a major disadvantage.

One problem with performing phtotocapacitance experiments inside the DAC results from the metal electrodes on the diodes. The metal overlayer prevents light from reaching the depletion layer of the sample directly. We have solved this problem by scattering the light in the pressure medium so light enters the Schottky barrier from the sides of the sample.[9] Unfortunately it is not possible to determine quantitatively the amount of light absorbed in this arrangement.

III. Results

We will discuss the results we obtained on several different defect systems to illustrate the kind of Physics one can learn using the DAC and capacitance measurements.

1. Pressure Induced DX center in GaAs:Si

The best example of how pressure can affect the property of defects in semiconductors through band structure changes is a deep donor known as the DX center. Further discussion on the DX centers can be found in the article by Suski in this volume.

A deep trap was discovered in 1977 by Lang and coworkers[10] in n-type AlGaAs alloys . One characteristic of this deep center was that its photoionization threshold (at about 1.0 eV) was about ten times larger than its thermal ionization energy.[11] Lang[12] explained this property by a very localized center with large lattice relaxation. They suggested that the center consisted of a complex of a donor atom and an unknown defect and as a result they labeled this center the DX center. The center was found only in AlGaAs alloys and not in pure GaAs at atmospheric pressure, so it was proposed that the complex involved an intrinsic defect, such as a vacancy, found mainly in alloys and much effort has been made to determine the nature of the intrinsic defect X in the DX center. In 1985 Mizuta et al.[13] applied pressure to n-type GaAs doped with Si using a Bridgman anvil device and discovered that at pressures exceeding 24 kbar, a deep donor with properties very similar to the DX center started to appear in the DLTS spectra. If this pressure-induced deep donor were identical to the DX center then the pressure experiment suggested that the DX centers in GaAlAs might not involve an intrinsic defect. Instead the Si donor undergoes a shallow to deep transformation as a result of conduction band structure changes.

A crucial test of whether the pressure-induced donor in GaAs:Si and the DX center in AlGaAs are identical is the determination of the photoionization threshold for the pressure-induced deep donor in GaAs. Li et al.[9] have measured the photoionization cross section σ of the deep donor in GaAs under pressure with a DAC. They loaded a Schottky barrier diode fabricated from the GaAs:Si into a DAC.

After the deep donors appeared under pressure, they are filled at room temperature at zero bias. The sample together with the DAC are then cooled to liquid nitrogen temperature in the dark. A reverse bias is applied to empty the donors. Due to an emission barrier of about 300 meV the rate of thermal emission of carriers from the deep centers is very small. The sample is next illuminated with monochromatic radiation. When the photon energy is sufficiently high, electrons are optically excited out of the deep centers and the optical ionization cross section can be determined from the change in the diode capacitance. The photoionization cross section measured in GaAs:Si under 33 kbar of pressure are shown as a function of photon energy in Fig. 2 (solid circles).

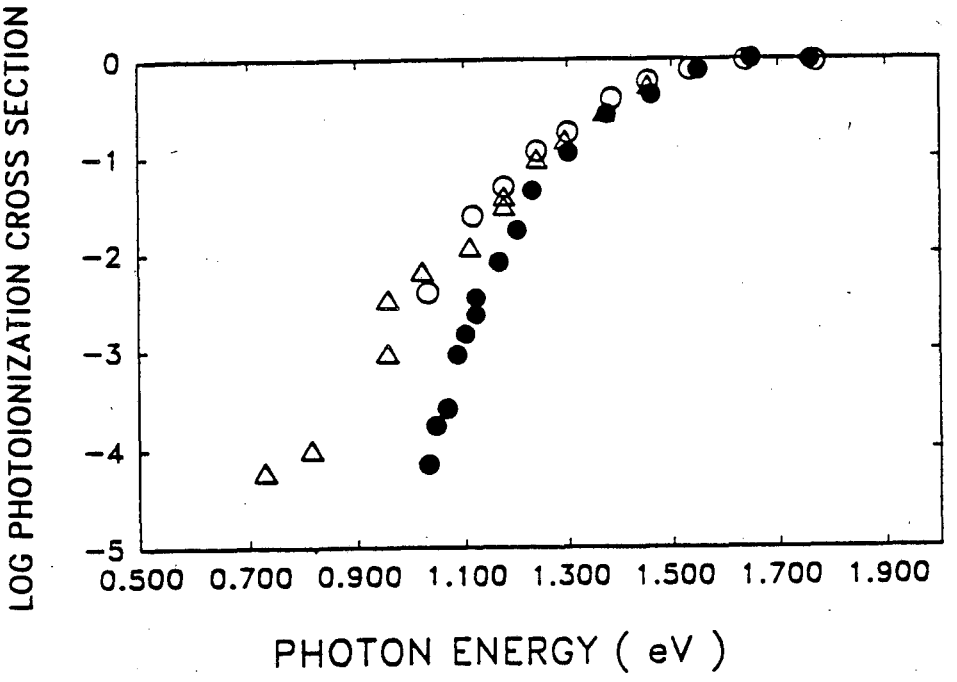

Fig. 2 Normalized photoionization cross section of DX centers in $Ga_{0.26}Al_{0.74}As$ at ambient pressure (open circles and triangles) from Refs. 14 and 15 compared with the photoionization cross section of the pressure-induced deep donor in GaAs measured under a pressure of 33 kbar (solid circles).

These results are compared with the photoionization cross section of the DX center measured in $Ga_{0.26}Al_{0.74}As$ at ambient pressure (open circles and triangles).[14,15] The similarity between the two sets of data provides strong evidence that the deep donor observed in GaAs under pressure is the same as the DX center discovered by Lang and coworkers. Since then many experiments have shown conclusively that the DX center with large lattice relaxation is a metastable resonant state in GaAs.[16] The effect of pressure and alloying GaAs with Al is to increase the energies of the conduction band minima at zone center and at the L point while decreasing the energy of the conduction band minima at the X point relative to the zone center minimum. Thus pressure or alloying lower the resonant DX state into the energy gap where it becomes the stable state. By comparing the effect of pressure and alloying on the

DX center in GaAlAs:Te, Shan et al.[17] found that the effect of 1 kbar is approximately equivalent to 1% of Al!

Discoveries of other interesting properties of the DX centers have also been made under pressure. As pointed out earlier, electrons have to overcome a barrier of about 300 meV in order to be emitted from the DX centers. This emission barrier height (E_e) was found to be sensitive to the chemical nature of its next nearest neighbors (nnn) for donors occupying Ga sites. We first notice that the E_e in GaAs:Si under pressure is only about 300 meV, much smaller than the value of over 400 meV reported in AlGaAs alloys.[18] Later Mooney et al.[19] found that DX center with no Al in nnn sites has E_e of 330 meV while DX centers with one Al and two Al nnn have higher values of E_e of 400 and 430 meV respectively. On the other hand in GaAs grown by liquid encapsulated Czochralski (LEC) method we found that the DX centers observed under pressure have smaller E_e of only 140-180 meV due to the presence of boron.[20] These results suggested that the DX center wave function extends at least to the nnn and furthermore some of the deleterious effects DX centers have on devices may be reduced by codoping with impurities such as boron.

2. Effect of Pressure on the P_b Center at Si/SiO_2 Interface

It is now well established that thermal oxidation of the (111) Si surface produces a paramagnetic defect near the Si/SiO_2 interface known as the P_b center.[21,22] Because of the importance of this defect to the Si MOS technology, much theoretical and experimental work has been devoted to determine the nature of this center. Based on EPR measurements it was proposed that the P_b center consists of a Si atom at the interface with a dangling bond aligned along the [111] direction perpendicular to the interface.[22] This model of the P_b center has been shown to be consistent with all the experimental results available on the P_b center. However, it was recently pointed out by Pantelides and coworkers[23] that experimental results in amorphous Si often attributed to Si with a dangling bond can also be explained by a fivefold coordinated Si atoms with a 'floating bond'. As an extension of this model it was suggested that the P_b center might also involve a floating bond rather than a dangling bond. Edwards[24] has pointed out that a definitive test of these competing models would be the pressure dependence of the P_b center. Edwards showed that compressive strain would cause the defect level to move towards the valence band in the dangling bond model by pushing the defect atom away from the interface. The opposite effect would occur for the floating bond model.

To test this idea, Johnson et al.[25] oxidized a p-type Si epi-layer deposited on a p^+-Si substrate by heating to 1100 °C in dry O_2. EPR measurement indicated that P_b centers with density of 10^{12} cm^{-2} were created by this process. MOS capacitors were fabricated by depositing Al electrodes on to the oxide film. The area of the gate electrode was approximately 170x170 μm^2 so the total number of P_b center was about $3x10^8$ in each device. Pressure was applied with a DAC using $CaSO_4$ as the pressure medium. The density of interface states due to the P_b center was determined by constant-capacitance voltage transient spectroscopy (VTS). Details of

this technique can be found in Ref. 26. The pressure dependence of the density of states of the P_b is shown in Fig. 3. The peak in the density of states shows a definite shift towards the valence band as the pressure is increased. The pressure

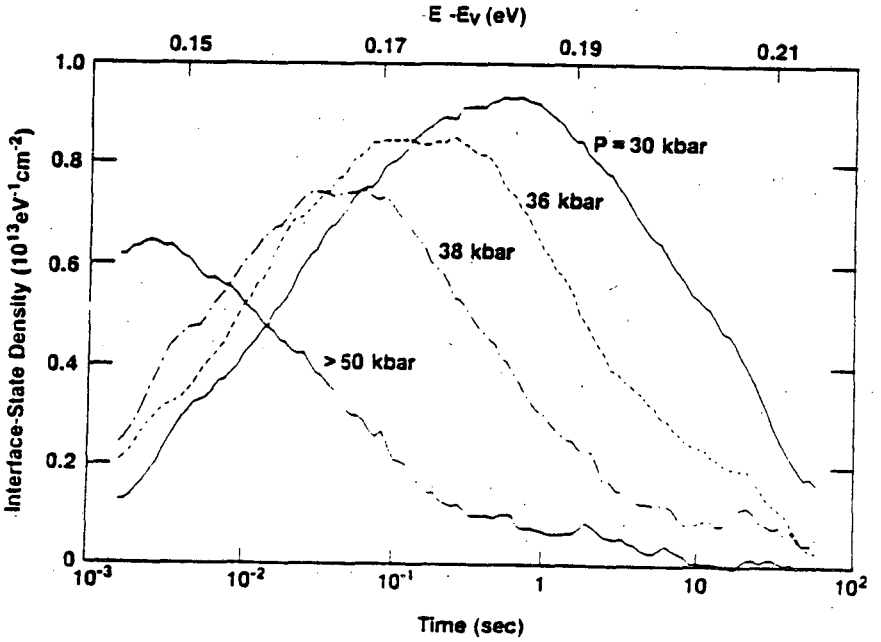

Fig. 3 Pressure dependence of interface state density associated with P_b centers at the Si/SiO_2 interface deduced from the gate voltage transients at constant capacitance.

coefficient of the peak was estimated to be -1.2 meV/kbar. Not only the sign of the pressure coefficient agrees with the prediction based on the dangling bond model but the order of magnitude of the pressure coefficient is also in good agreement with the value of -1.7 meV/kbar predicted by Edwards.[27] To our knowledge this is the first application of the DAC to study the pressure dependence of interfacial defects.

3. Effect of Pressure on Schottky Barrier Height of GaAs

Schottky barriers (SB) formed on the surface of compound semiconductors have been the subject of numerous investigations. Although it has been established that SB are the result of pinning of the Fermi level to some states within the band gap, the microscopic nature of these gap states is still unknown at present. A large variety of native defect states such as vacancies, antisites and EL2, have been suggested as the origin of these gap states.[28-30] One way to test the validity of these proposals in GaAs is to measure the pressure dependence of SB on GaAs and compare the result with the pressure dependence of different types of deep levels induced by native defects. The pressure coefficients of many deep levels associated with native defects in GaAs have been either measured experimentally[31,32] or calculated theoretically.[33]

The pressure experiment was performed inside the DAC by Shan et al.[34] on SB diodes fabricated by depositing Pt on n-type GaAs. The SB height ϕ_B was determined from the I-V characteristics of the forward biased diode. The resultant variation in ϕ_B with pressure (P) is shown in Fig. 4. The pressure dependence is nonlinear and

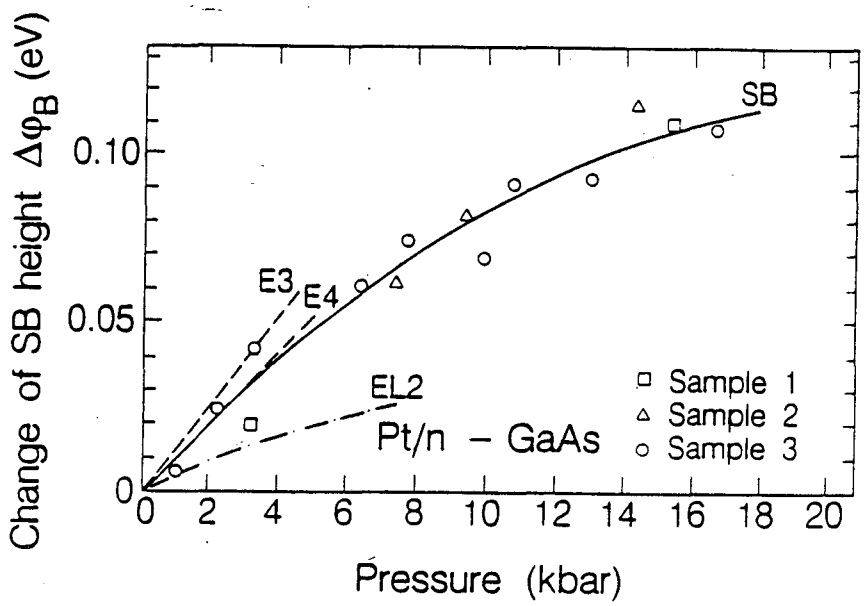

Fig. 4 Variation of the SB height with pressure for three different Pt/GaAs diodes. For comparison the pressure dependence of three deep levels in GaAs: EL2, E_3 and E_4 are also shown.

can be fitted well with a quadratic equation:

$$e\phi_B(P) = e\phi_B(0) + \alpha P + \beta P^2 \qquad (1)$$

with $e\phi_B(0)=0.703$ eV, $\alpha=11$ meV/kbar and $\beta=-0.26$ meV/kbar^2. The linear coefficient α agrees very well with the pressure coefficient of the band gap of GaAs.[35] Although the nonlinear coefficient is about three times larger than the nonlinear pressure coefficient of the band gap,[35] considering the large uncertainty in β one can conclude that whatever pins the Fermi level follows the valence band as a function of pressure. In Fig. 4 we show also the pressure dependence of some intrinsic defect levels in GaAs.[31,32] While some defect levels such as E_3 and E_4 have pressure coefficients very similar to that of the SB, our results do not conclusively identify these defects as necessarily responsible for the formation of the SB. However, our result excludes defects whose pressure coefficients differ significantly from that of the SB height. The microscopic structure of the SB is still a unresolved problem. The pressure dependence of SB is an important piece information which will help to solve this problem.

IV. Conclusion

With the successful implementation of electrical and electro-optical measurements inside the DAC, we can say that it is now possible to study defects in semiconductors under high pressure inside the DAC with all the known available characterization techniques with the exception of perhaps EPR.

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