Band-Structure Studies on Silicon Using a Metal-Oxide-Semiconductor Junction*

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Photoemission from solids into a vacuum has hitherto been used in the study of the band structure of solids. Photoemission from one solid into another can also be used to study the band structure. Photoelectric emission from silicon into oxide in a metal-oxide-semiconductor (MOS) geometry is used in this paper for the study of the band structure of silicon. The photoelectric threshold energy is reduced by bias heat treatment of the MOS structure, analogous to the cesiation of the silicon surface, to reduce the work function in vacuum emission studies. In the region below 5.8 eV, we observe four peaks at 3.5, 4.2, 5.0, and 5.7 eV. These results are compared with those observed by Gobeli and Allen in vacuum-emission studies and with the theoretical calculation of Brust. It is concluded that the photoelectric investigation using a MOS geometry is a convenient tool for the study of the band structure of semiconductors.

PHOTOEMISSION from solids into vacuum has come to be recognized in recent years as one of the tools for the study of the energy band structure of solids.[1] Photoemission from silicon surfaces into vacuum has been studied by three groups. Spicer and Simon[2] and Van Laar and Scheer[3] observed photoemission from cesiated silicon surfaces. Allen and Gobeli[4,5] reported photoemission studies from atomically clean surfaces. The latter group also reported structures in the spectral yield which could be accounted for by direct transitions based on the theoretical calculation of Brust.[6] Analogously, photoemission from one solid into another also should reveal structures corresponding to the energy band transitions of the solid where the photoexcitation takes place. In this paper, we report structure in the photoelectric yield of emission of electrons from silicon into oxide in metal-oxide-semiconductor (MOS) geometry. In the region below 5.8 eV for photon energies, we observe peaks at 3.5, 4.2, 5.0, and 5.7 eV. Three of these peaks are essentially the same as those observed by Allen and Gobeli[5] at 3.5, 4.8, and 5.7 eV, from their measurements on degenerate p sample. In this paper, we use the theoretical calculations of photoelectric yield made by Brust on silicon to interpret our results, as was done by Allen and Gobeli. We point out in this paper that MOS geometry and photoemission into solid (oxide) form a convenient technique for band-structure studies, especially in view of the fact that the photo threshold can be progressively reduced by bias heat treatment.

Pioneering work on photoemission in MOS structure was made by Williams[7] and was followed by Goodman[8–10] and Deal *et al.*[11] Snow *et al.*[12] observed changes in the capacitance-voltage (CV) characteristic of MOS structure when the sample was heated under a bias voltage, usually referred to as bias heat treatment. This shift in CV characteristic was explained as due to accumulation of positive ions near the silicon-oxide interface when the metal is biased positive during the bias heat treatment. In an earlier paper,[13] we reported a reduction in the photoelectric threshold for emission of electrons from silicon into oxide due to an accumulation of positive ions near the silicon-oxide interface. Analogous to cesiation of the silicon surface to lower the work function in vacuum emission studies, we use in our present study the bias heat treatment to observe structure in the yield due to optical transitions terminating in lower final energy states. Also, by progressively increasing in small increments the bias voltage between successive bias heat treatments, it is possible to lower the threshold energy gradually from the initial value corresponding to random distribution of positive ions in the oxide to its final value corresponding to all the ions being concentrated near the silicon-oxide interface.

Measurements were carried out on MOS structures consisting of a 5000 Å-thick oxide layer sandwiched between the (111) face of p-type degenerate silicon and a $\sim$200 Å-thick transparent gold layer. The details of the experimental arrangement for the photoelectric measurement are similar to those reported earlier[13,14] except for the angle of incidence of the beam of light. Curve 1 in Fig. 1 gives the yield curve obtained in a sample where the positive ions are randomly distributed corresponding to a photoelectric threshold energy of

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TABLE I. Band to band transitions in silicon.

Brust's prediction for 2.5-eV barrier height (eV)	Phillip and Taft's measurement (eV)	Allen and Gobeli's measurement (eV)	Our experiment (eV)	Transition
3.5	3.5	3.5	3.5	$\Gamma_{25'} \rightarrow \Gamma_{15}$
3.9	4.3	···	4.2	$\Gamma_{25} \rightarrow \Gamma_{21'}$
5.2	···	4.8	5.0	$L_{3'} \rightarrow L_3$
5.8	5.5?	5.8	5.7	?

nearly 4.2 eV. We observe a peak at 5.7 eV in this curve. However, this curve must be corrected for interference effects,[8] since optical interference in the sandwiched layer of oxide produces a series of minima and maxima in the absorbed light as the photon energy is varied. To eliminate the interference effects in the plot of the photoelectric yield versus photon energy, it is required (following Goodman[10]) to plot photoelectric current per absorbed photon instead of photoelectric current per incident photon. Towards this goal, an auxiliary experiment was carried out. The light reflected off the MOS sample was measured as well as the incident light. The ratio r of reflected to incident light was obtained as a function of photon energy. Curve 1 in Fig. 1, which gives the photoelectric yield per incident photon, is divided by $1-r$ to obtain the photoelectric yield per absorbed photon and this is plotted as curve 2 in Fig. 1. We notice two peaks at 5.1 and 5.7 eV in this case. If we consider the theoretical calculation of Brust reported in Ref. (5) for a barrier height of 4 eV, two peaks are predicted at 5.1 and 5.9 eV, and our measurement compares well with the theoretical prediction.

To effect a reduction in the photoelectric threshold energy due to a combination of band bending in silicon near the oxide interface and Schottky reduction of the interface barrier height, we subjected the MOS sample to a bias heat treatment. During the bias heat treatment, the sample was heated for 30 min under a positive bias voltage applied to the gold layer. Then, the

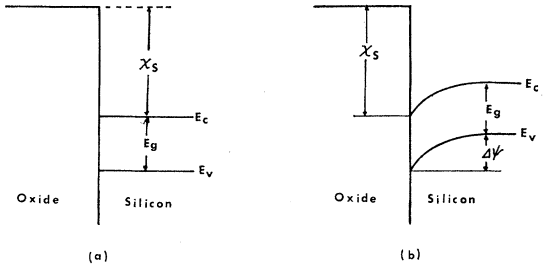

FIG. 2. (a) Energy-band diagram before bias heat treatment; $h\nu_{\text{threshold}} \approx \chi_s + E_g$; (b) energy-band diagram after bias heat treatment; $h\nu_{\text{threshold}} \approx \chi_s + E_g - \Delta\psi$.

sample was allowed to cool down to room temperature and the photoelectric measurement was conducted. A reduction in the photoelectric threshold energy was observed as reported earlier[13] and the amount of reduction depended on the bias voltage and the duration of the heating process for a given temperature. The reduction in the photoelectric threshold can be explained as being due to the migration of mobile positive ions towards the silicon interface during the bias heat treatment. The accumulation of positive ions near the silicon interface produces bending of the band in silicon. The electrons generated in regions of silicon deeper than the distance, over which band bending occurs would be more energetic than the electrons generated close to the interface, by the amount equal to the amount of band bending. If the distance over which the bending of the band occurs is small compared with the escape length of the excited electrons, then the photocurrent will be comprised mainly of the more energetic electrons and this will correspond to an apparent reduction in the interface barrier height by an amount equal to the band bending. This can be understood by reference to Fig. 2 where the energy band diagram of the MOS structure is shown before and after positive bias heat treatment. In addition, the barrier height at the interface is also reduced by the Schottky effect due to the electric field produced by the positive ions

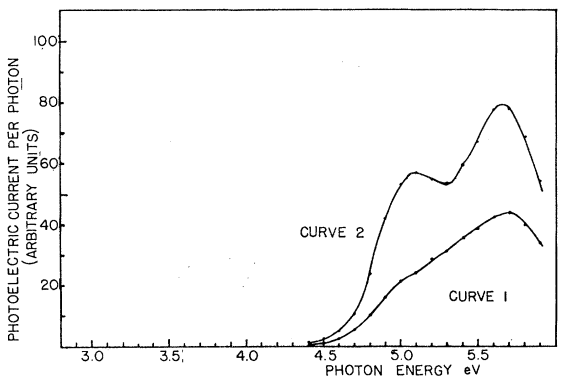

FIG. 1. Photoelectric yield of p-type degenerate silicon with interface barrier height equal to 4.2 eV. Curve 1 gives the yield per incident photon. Curve 2 gives the yield per absorbed photon.

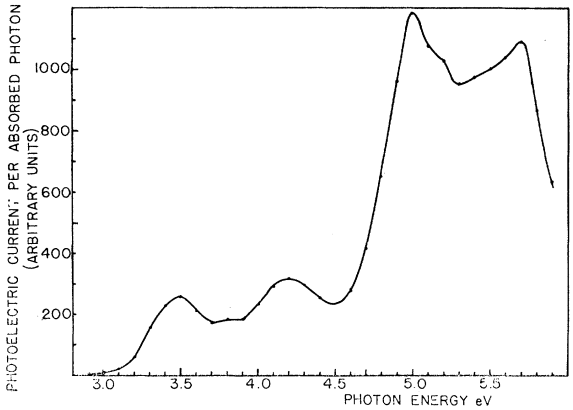

FIG. 3. Photoelectric yield of p-type degenerate silicon with interface barrier height equal to 2.4 eV.

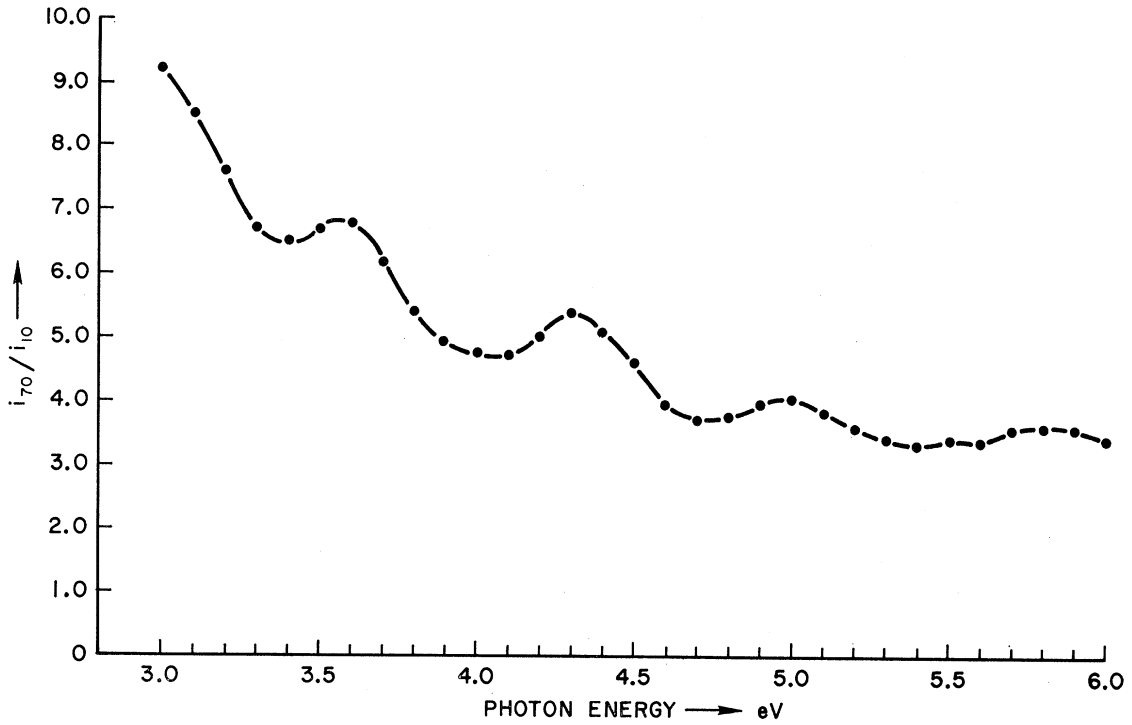

FIG. 4. Plot of the ratio of the photoelectric yield i_{70}, at $V_G=70$ V to the photoelectric yield, i_{10}, at $V_G=10$ V.

accumulated near the silicon interface.[15] However, the reduction due to the Schottky effect is smaller than that due to the band bending in silicon.

The reduction in the photoelectric threshold from the initial value can be made in small increments by using increasing bias voltage during successive bias heat treatments. The reduction will continue until all the positive ions are piled near the silicon interface. In these experiments, it was found that a bias voltage of 15 V applied for 30 min at 200°C was found sufficient to produce the maximum possible reduction in the photoelectric threshold voltage. The number of mobile positive ions in our sample was estimated by integrating the transient ionic current during the bias heat treatment and this was of the order of $5\times10^{12}/\text{cm}^2$. The photoelectric threshold after the bias heat treatment was obtained by plotting the square root of the photocurrent as a function of photon energy. The threshold was found to be reduced to a value of approximately 2.4 eV and the linear slope in the plot of the square root of the current shows the optical transitions to be indirect. Figure 3 gives the plot of photoelectric yield per absorbed photon (corrected for interference effects) after the positive-bias heat treatment. Four peaks are observed in this case as mentioned earlier. Figure 3 is very similar to Allen and Gobeli's measured yield plotted in Fig. 11 in Ref. 5. However, only three peaks are observed by Allen and Gobeli. Brust's calculation of yield for a barrier height of 2.5 eV predicts four peaks, as summarized in Table I. Table I also lists the peaks observed in the plot of the extinction coefficient of Phillip and Taft.[16] The identification of the transitions are taken from the work of Brust, Cohen, and Phillips.[17]

Note added in proof. It has been pointed out by Powell[18] that it is not sufficient to correct the photoelectric yield by a factor $(1-r)$. The correction factor should be $T=1-r-A$, where T is the fraction of the incident light absorbed by silicon and A is the fraction absorbed by the gold layer. However, it is not possible to measure A directly.[19] In our experiment, therefore, it is possible that the measured values of peaks corresponding to direct transitions at symmetry points may be in slight error. Since it is not possible to correct for interference completely by reflectance measurements, the following method of verification was adopted in which interference effects were completely eliminated.

The photoelectric threshold energy is reduced in the bias heat treatment due to band bending in silicon. It is also possible to bend the bands in silicon by applying a large positive gate voltage V_G to the gold layer. For a given initial amount of band bending in silicon, a further band bending can be effected with a large V_G. Photoelectric measurements were made successively

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with $V_G=10$ V and $V_G=70$ V after the bias heat treatment with a bias voltage of +5 V to the gold layer. At $V_G=70$ V, the photoelectric threshold is less than at $V_G=10$ V and the photoelectric yield at $V_G=70$ V should therefore reveal more structures due to direct transitions than the yield at $V_G=10$ V. However, the structure due to interference is present in both the yields. If the photoelectric yield, i_{70}, at $V_G=70$ V is divided by the photoelectric yield, i_{10}, at $V_G=10$ V, then the resulting curve will be devoid of structures due to interference but will show only structures due to direct transitions. In Fig. 4, we have plotted i_{70}/i_{50} and this curve clearly shows peaks at 3.5, 4.3, and 5.0 eV. In this experiment, we did not observe any distinct peak at 5.7 eV because the terminal state for the 5.7 eV transition was possibly higher than the interface barrier height to start with and, as such, this transition did not increase in strength with band bending. The observation of the peaks at 3.5, 4.3, and 5.0 eV is in good agreement with our results given in Table I.

This experiment has demonstrated that the photoelectric technique in MOS structure is a very convenient tool for studying the energy band diagram of silicon. The attractive feature of this technique lies in the ability to vary the photoelectric threshold gradually by bias heat treatment. However, for this to be possible, the oxide should be fairly contaminated so that there are mobile ions of the order of $10^{12}/cm^2$ or larger. The disadvantage in this method lies in the fact that only degenerate samples will exhibit appreciable shifts in photoelectric threshold. The reason for this is that the distance over which band is bent in silicon is much larger (larger than the optical absorption length and the escape length) for nondegenerate samples than that in degenerate samples.

This method can be extended to the study of the band structure of other semiconductors provided a suitable insulator in MOS geometry can be found. This technique is also convenient for extension to the study of band structure at lower temperatures.

PHYSICAL REVIEW B VOLUME 1, NUMBER 2 15 JANUARY 1970

Room-Temperature Conductivity Anisotropy and Population Redistribution in *n*-Type Silicon at High Electric Fields

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Theoretical expressions have been derived for the high-field mobility of carriers in *n*-type Si for any arbitrary direction of field. The distribution function of the electrons in a valley has been assumed to be Maxwellian, and scattering by intravalley acoustic and two types of intervalley phonons have been considered. The conductivity anisotropy for room temperature obtained from theory is of the same order as found experimentally. The population ratio is, however, found to be in disagreement with the values obtained from the analysis of experimental results. A plausible explanation for this disagreement is also presented.

I. INTRODUCTION

EXPERIMENTAL results of high-field conductivity of *n*-type Si at different lattice temperatures are widely reported in the literature.[1–12] A small anisotropy is found in the conductivity characteristics obtained by the conventional methods, at room temperature.[4,11]

A theoretical analysis of the conductivity of *n*-Si at 77°K has been done by Asche and Sarbej[5] and by Asche *et al.*[6] In their analysis the Boltzmann equation was solved by a variational method assuming scattering by acoustic intravalley and two types of intervalley phonons. The characteristic phonon temperatures and coupling constants were taken according to Long.[16] Experimental results for electric field applied along [111] direction were compared with the theory and the agreement was found to be satisfactory. In a later analysis,[6] assuming Maxwellian distribution and including an additional intervalley phonon at 720°K, Asche *et al.* obtained the conductivity characteristics for the [100] direction at 77°K. The calculated characteristics were found to be in agreement with experiment.

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