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CORRELATION OF ELECTRICAL PROPERTIES OF a-SiH_x MIS SOLAR CELL STRUCTURES WITH THE STATE OF OXIDATION OF THE INTERFACE

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Abstract.-The collection efficiency, \( \eta \), for strongly absorbed light and the open circuit voltage, \( V_{oc} \), in a-SiH_x MIS solar cell structures are enhanced by the presence of a thin (\(< 20\AA\)) oxide layer at the metal/semiconductor interface. We find that the oxide layer causes an increase in the built in potential which accounts for the enhanced \( V_{oc} \). To account for the enhancement in \( \eta \) requires, in addition, for the semiconductor/metal interface to act as a reflecting barrier for electrons.

Introduction.- It is well known that the photovoltaic behavior of Schottky barrier solar cells can be drastically modified by the incorporation of a thin insulating layer between the metal and the semiconductor. Metal-insulator-semiconductor (MIS) structures have been studied extensively for the case of crystalline semiconductors (1). More recently MIS structures have been used in the case of amorphous silicon to enhance the open circuit voltage, \( V_{oc} \), of solar cells (2-4). Another beneficial effect of the insulator layer that has been observed in hydrogenated amorphous silicon (a-SiH_x) MIS structures is the enhancement in the collection efficiency, \( \eta \), for carriers generated by strongly absorbed light (5). In this paper we shed light on the mechanism of enhancement of \( V_{oc} \) and \( \eta \) in a-SiH_x MIS structures. We use Auger Electron Spectroscopy (AES) to characterize the state of oxidation of the a-SiH_x surface. Measurements of the internal photoemission and the forward I-V characteristics show that the enhancement in \( V_{oc} \) is due to an increase in the built-in potential, \( V_b \), in the semiconductor, while most of the enhancement in \( \eta \) results from the semiconductor/insulator interface acting as a reflecting barrier for electrons.

Results.- The a-SiH_x films were prepared by RF glow discharge decomposition of SiH_4 under conditions described previously (6). The substrates were 7059 glass with a 1000\AA thick evaporated Cr film. A 5000\AA thick phosphorous doped SiH_x film formed ohmic contact to the undoped SiH_x film which was typically 1\mu m thick. When we wished to achieve an intimate metal-semiconductor contact, we either transferred the films within several minutes after preparation to the vacuum system in which metal contacts (2mm\(^2\) Pd or Pt dots about 100\AA thick) were evaporated, or the films were etched in buffered HF and rinsed in deionized water just prior to metallization. No significant differences were found in the electrical properties of the MIS structures formed by the two methods. The oxidations were performed in oxygen at 300\degree C prior to the evaporation of the semitransparent metal contacts.

To characterize the surfaces of our a-SiH_x films, we prepared samples suitable for surface analysis. These samples were prepared and treated (etched or oxidized) identically as those used for the electrical measurements. After the treatment, the samples were introduced within 15 minutes, via a fast introductory system, into an ultra-high vacuum chamber for the surface analyses. AES was used for elemental surface characterization. U.V. photoelectron spectroscopy along with Si Auger line shape were used to characterize the nature of the oxide. We find that freshly etched surfaces exhibit an Auger \( dN(E)/dE \) peak near 90 eV characteristic of non oxidized Si. The detailed line shape is qualitatively similar to that of clean silicon. The ratio of the intensities of the oxygen 510 eV transition to that of the silicon 90 eV transition is between 0.03-0.10. By sputter cleaning we succeeded to reduce this ratio further to \( \sim 0.005 \). In addition to oxygen we usually also observed traces of carbon.

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near 270 eV. Upon oxidizing the surface, the amplitude of the oxygen signal increased while the amplitude of the silicon line at 90 eV decreased. At the same time the silicon Auger transition started to develop features below 80 eV characteristic of oxidized Si (7). The detailed shape of the silicon Auger transition is shown in Fig. 1 for three different conditions of the a-SiHx surface: sputter cleaned (A), oxidized (B), and heavily oxidized (C). We can follow here the decrease of the 90 eV peak and the development of a peak near 75 eV. We find that the ratio of the amplitudes of the two peaks, which we label $SiO_2(75)/Si(90)$, is a good measure of the state of oxidation of the surface. This ratio is quite insensitive to the presence of the other contaminants (mainly carbon) at the surface which may affect the $O(510)/Si(90)$ ratio. We thus use the ratio $SiO_2(75)/Si(90)$ as a phenomenological measure of the oxidation. With certain assumptions (8) one can convert this ratio to oxide thickness, yielding maximum values of up to 30 Å for our oxide layers.

Collection efficiency measurements were made with monochromatic light flux of $10^{13}$ photons/cm$^2$sec. Details of the technique have been published (9). The collection efficiency $\eta(\lambda)$ (defined as the ratio of charge carriers collected to photons transmitted through the top metal contact) is shown as a function of wavelength $\lambda$, in Fig. 2 for two MIS structures. The data were obtained under short circuit current conditions, on a cell with intimate metal-semiconductor contact and on one in which the SiHx film was exposed to oxygen for 30 minutes. The line in the figure is theoretical and was calculated using the model of Gutkowicz-Krusin (10) with the characteristic width of the space charge region, $X_0$ and the hole diffusion length, $L_P$ as best fit parameters. An absorbing boundary was used in the calculation i.e., every carrier reaching the contact is assumed to be extracted. The calculated curve can be seen to reproduce all of the features of the experimental data and, in particular, the decrease of $\eta(\lambda)$ at the small values of $\lambda$. This decrease is due to the back diffusion of the electrons photogenerated close to the contact and it is the feature which is most strongly affected by a thin oxide layer. We have investigated a number of a-SiHx samples having different densities of gap states. We find (11) that the values of $\eta(\lambda)$ at short wavelengths ($\lambda > 0.4\mu m$) are essentially determined by the surface electric field which to a good approximation is $V_o/X_0$ and depends both on the metal contact and on the density of gap states. However, invariably we find that upon oxidation, $\eta(\lambda)$ increases at short wavelengths.

In Fig. 3 we plot the $V_o$ values, obtained with 100mW/cm$^2$ of tungsten white light, as a function of the $SiO_2(75)/Si(90)$ ratio for several Pd/a-SiHx structures. We notice that $V_o$ increases monotonically with the degree of oxidation up to about 0.7 volt where it saturates. This saturation was well established on many samples; in Fig. 3 we only plotted results on samples where we also measured the AES spectra. The points at the lowest oxygen coverage correspond to etched samples and represent...
Fig. 3. Open circuit voltage, $V_{oc}$, as a function of the ratio of the SiO$_2$ (75) peak to the Si(90) peak.

Fig. 4. Plot of $\eta$ vs. photon energy for an etched and two oxidized Pd/a-SiH$_x$ structures. The values of the intercepts of the straight lines corresponding to the barrier heights, $\phi$, are 1.04, 1.13 and 1.15 eV.

Fig. 5. Current-voltage characteristics under far forward bias conditions for the etched and oxidized (I) samples of Fig. 4. Extrapolated values of $V_o$ are marked in the figure.

Discussion.- In order to unambiguously correlate the state of oxidation with the electrical properties of the MIS structures we found it necessary to characterize the surfaces by AES. We discovered, somewhat to our surprise, that exposure to oxygen for a given amount of time did not always reproduce the same degree of oxidation. This may possibly be due to the presence of minute quantities of impurities which could catalyze the oxidation process.

The experimental results provide evidence that thin oxide layers (< 20Å) in a-SiH$_x$ MIS structures increase the barrier height $\phi$. Practically all of the increase in $\phi$ appears as an increase in the built-in potential, $V_o$. This suggests that the increase in $\phi$ and $V_o$ is due to transfer of electrons oxygen coverages close to a monolayer. We also performed measurements on Pt/a-SiH$_x$ MIS structures; the value of $V_{oc}$ corresponding to the etched surfaces was appreciably higher ($\sim 0.55$ to $0.60$ V) than for the comparable Pd structures while the maximum value was still $V_{oc} \sim 0.7V$.

To evaluate the barrier heights, $\phi$, of the MIS structures we measured the internal photoemission (12) (from the metal into the a-SiH$_x$) using low photon energies (hv below 1.5 eV). In Fig. 4 we show typical results for the collection efficiency, $\eta$, as a function of hv for an etched and two oxidized Pd/a-SiH$_x$ MIS structures. As can be seen in the figure, the data follow the standard equation for metal-semiconductor Schottky barriers,

$$\eta^{1/2} = A(hv - \phi),$$

where $A$ is a constant. The values of $\phi$ derived from the data are marked in the figure. The corresponding differences in $V_{oc}$ between these etched and oxidized samples were 0.10V and 0.13V for oxidized samples (I) and (II), respectively; in good agreement with changes in $\phi$. We were unable to measure barrier heights above $\sim 1.2$ eV because the internal photoemission became too small and was obscured by photogeneration from gap states (12). The values of $\phi$ for the Pt/a-SiH$_x$ etched samples were between 1.1 and 1.2 eV, consistent with the higher $V_{oc}$ values for these samples. Because of the experimental limitations we did not measure $\phi$ for the Pt/a-SiH$_x$ oxidized samples.

To determine the built-in potential, $V_o$, we measured the far forward bias I-V characteristics. Although there may be some uncertainty in the absolute value of $V_o$ derived by this method, it is quite suitable for measuring changes in $V_o$ (13). In Fig. 5 we show the far forward bias characteristics of the etched and oxidized (I) samples of Fig. 4. The change in the extrapolated values of $V_o$ (marked in the figure) is 0.1V, in close agreement with the corresponding change observed in $\phi$.
from the semiconductor into acceptor-like surface states associated with the presence of the oxide layer. Such an interpretation is consistent with our experimental observation that the diode quality factors (2) for our thin oxides (≤ 20Å) remained equal to unity. For thicker oxides the diode quality factors were larger than unity, indicating that some of the built-in potential drop occurs across the oxide.

While the increase in $V_0$ fully accounts for the increase in $V_{oc}$, it is not sufficiently large to explain the observed enhancement of $\eta$ for strongly absorbed light. To further reduce the back diffusion of electrons to the metal contact, the oxide layer has to act as a partially reflecting barrier. The origin of the reflecting barrier is likely to be due to a misalignment of the a-SiH$_x$ and oxide conduction bands. On the other hand, it appears from our data that the hole transport is not significantly affected by the oxide.

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References.-