Solid State Communications, Vol. 23, pp. 421 - 424, 1977. Pergamon Press. Printed in Great Britain.

SURFACE STATES AND BARRIER HEIGHTS OF METAL-AMORPHOUS SILICON SCHOTTKY BARRIERS*

C. R. Wronski and D. E. Carlson

RCA Laboratories, Princeton, New Jersey 08540

(Received 27 May 1977 by E. Burstein)

The barrier heights, ϕ_B, of Schottky barriers formed between Al, Ni, Cr, Pd, Au, Rh, and Pt metal films and undoped discharge-produced amorphous silicon (a-Si) have been measured. The dependence of ϕ_B on the metal work function, ϕ_M, has been characterized for values of ϕ_M between ~4.0 and 5.5 eV. Experiments were performed to compare the effects of surface states on ϕ_B of both the undoped (n-type) amorphous and n-type single crystal Si. These effects of surface states are very similar, indicating similar densities and energy distributions of surface states. The densities of surface states on a-Si are found to be $\gtrsim 10^{13} cm^{-2} eV^{-1}$ which result in the pinning of ϕ_B to values $\gtrsim 0.7$ eV even with ϕ_M as low as 4.0 eV.

Recently metal-amorphous silicon (a-Si) Schottky barrier structures exhibiting nearly ideal diode characteristics have been reported by Wronski, Carlson, and Daniel.[1] Such junctions formed by the evaporation of thin metal films onto discharge-produced a-Si have been utilized in fabricating efficient solar cells[2] and in evaluating the electronic properties of a-Si.[3] The Schottky barriers can be characterized in terms of the same parameters as those on single crystals and their barrier heights can be independently determined by I-V, capacitance, and photovoltaic measurements.[3] Although extensive measurements have been carried out on a-Si in recent years,[4] the nature of evaporated metal contacts has received little attention even though such contacts have been extensively used in electrical measurements.

We report here on studies carried out on metal/a-Si Schottky barriers formed with metals having a wide range of work functions (~4.0 to 5.5 eV). The metals used were evaporated onto both n-type a-Si and single crystal Si so that by measuring the various metal barrier heights the effects of surface states on a-Si could be directly compared to those of single crystal Si. Such information about surface states is highly desirable since they play an important role in the interpretation of results obtained with insulator/a-Si junctions.[5] The results reported here indicate surface state densities which are close to those found from previous studies on single crystal Si.[6]

In metal-semiconductor junctions the barrier height, ϕ_B, depends on the electron affinity of the semiconductor, χ, the metal work function ϕ_M, and the semiconductor surface states. These surface states are found to play an important role in determining ϕ_B of metal single crystal Si barriers and their density can be estimated from the dependence of ϕ_B on ϕ_M which is given by[7]

$$\phi_B = C_1\phi_M + C_2 \qquad (1)$$

In Eq.(1) $C_1 = \varepsilon_i/(\varepsilon_i + q\delta D_S)$ where D_S is the density of surface states ($cm^{-2}eV^{-1}$), δ is the thickness and ε_i is the dielectric constant of any insulating film present at the interface; and C_2 is related to density of surface states, their energy distribution, and the position of the Fermi level at the surface prior to the formation of the metal-semiconductor contact. It can be seen that when there are no surface states present, $D_S = 0$, so that $C_1 = 1$ and any change in ϕ_B is directly proportional to any change in ϕ_M.

In order to evaluate the effects of surface states on ϕ_B it is necessary to be sure that the nascent oxide at the interface is thin enough to allow the use of the above analysis and also that the barrier height measurements are accurate. Little is known about the oxidation of a-Si in terms of the thickness and properties of the oxide films that are formed on it upon exposure to air. However, deductions can be made about the thickness of the oxide at a metal-semiconductor interface from I-V and capacitance-voltage (C-V) characteristics of the junction.[8]

The separation of charge at the interface results in a potential drop across the insulating film, V_i, and the semiconductor, V_o, which is given by

$$\phi_B = V_o + V_i + E_f + kT/q \qquad (2)$$

*Research reported was prepared for the Division of Solar Energy of the U. S. Energy Research and Development Administration under Contract No. E(04-3)-1286, and RCA Laboratories, Princeton, New Jersey.

where kT/q is 26 mV at 300 K and E_f is the distance of the Fermi level from the conduction band in the bulk of the semiconductor. The potential drop V_i depends on the thickness, δ, of the insulator, the electric field at the semiconductor surface, and the charge in the surface states. For $\delta \lesssim$ 10-20 Å, V_i is smaller than kT/q, and the barrier characteristics become almost indistinguishable from those predicted for ideal metal-semiconductor contacts.

The I-V characteristics of such junctions follow the relation for forward bias current densities, J, as a function of voltage, V, given by:

$$J = J_o \left[\exp\left(\frac{q}{kT}\,\frac{V}{n}\right) - 1\right] \qquad (3)$$

where J_o is the saturation current density and n is the diode quality factor which in the absence of recombination in the junction is very close to unity. The saturation current density is given by

$$J_o = B \exp\left(-\frac{\phi_B}{kT}\right) \qquad (4)$$

where B is given by the diffusion theory of metal semiconductor rectification in the case of a-Si and Richardson's equation in the case of single crystal Si. In far forward bias, where currents become limited by the resistance in series with the barrier the expression for J becomes[9]

$$J \simeq \frac{(V-V_o)}{R_S} \qquad (5)$$

where, in presence of an ohmic or low resistance contact, R_S is the resistance per unit area due to the bulk resistivity of the semiconductor. The C-V characteristics obtained with a small signal ac capacitance measurements of the barrier region as a function of dc bias are given by:

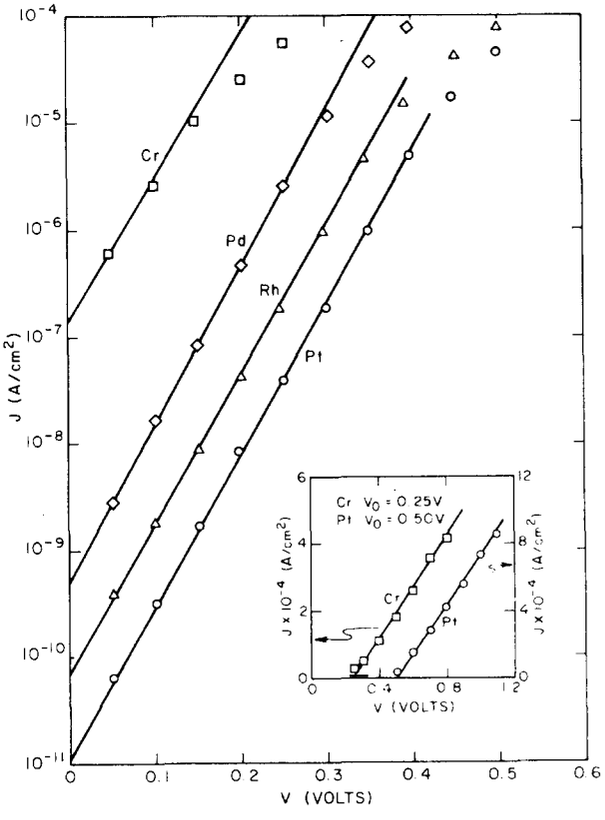
$$\frac{1}{C^2} = \frac{8\pi}{\varepsilon q}\,\frac{(V-V_o - kT/q)}{N} \qquad (6)$$

where ε is the dielectric constant and N is the space charge density in the barrier.

Insulating films at the interface, which result in significant values of V_i an which limit the charge transport between the semiconductor and metal, result in values of n significantly larger than unity[8] and lead to $1/C^2$ vs V plots which result in intercepts much greater than $V_o - kT/q$.[10] In such cases also disagreement is expected between these values and those obtained from the extrapolated far forward bias currents. In the absence of such discrepancies an upper limit of ~20 Å can be placed on the effective thickness of a nascent oxide and Eq.(1) can be used to determine the effect of surface states on ϕ_B.

The Schottky barriers were formed on undoped (n-type) a-Si and n-type single crystal Si by vacuum evaporation of Al, Ni, Cr, Pd, Au, Rh, and Pt metal films. These films were evaporated at a residual pressure of ~10^{-6} Torr onto both kinds of silicon at room temperature. The a-Si structures used were similar to those reported earlier,[1] consisting of undoped a-Si films, ~1 μm thick. The undoped a-Si was deposited from a dc discharge in silane onto substrates at ~320-350°C. These substrates consisted of ~300 Å thick phosphorus-doped a-Si on stainless steel forming ohmic or low resistance contacts to the undoped a-Si. The n-type Si wafers were 1-3 Ω-cm, had a (111) orientation and Al contacts sintered at ~400°C. Just prior to the evaporation of the semitransparent metal films both the a-Si films and single crystal Si were etched in buffered HF after prior chemical cleaning. Arrays of metal dots, having areas from 5×10^{-3} to 2×10^{-2} cm^2 were evaporated onto both the a-Si and crystalline Si substrates. To take into account any changes that occur between different evaporations of the same metal as well as differences between different a-Si samples, the different metals were evaporated onto sections of the same a-Si substrate as well as other a-Si films. The Schottky barrier heights and their dependence on the metal work function were determined using I-V capacitance and photovoltaic characteristics[3] on both a-Si and single crystal diodes.

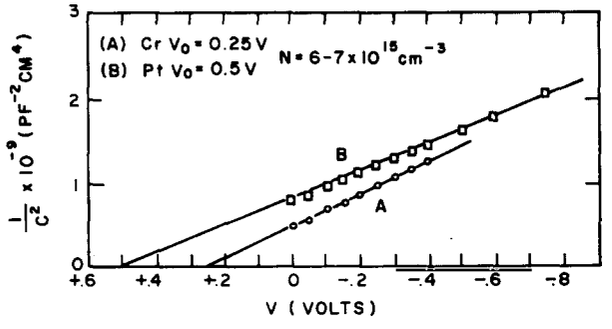
The I-V and C-V characteristics of both the a-Si and single crystal Si Schottky barriers were in agreement with Eqs.(3) to (6). There was also good agreement between the values of V_o obtained by means of capacitance and far forward bias measurements. In Fig. 1 is shown the exponential behavior, predicted by Eq.(3) that was obtained with Cr, Pd, Rh, and Pt Schottky barriers on a-Si. Also shown in the inset are the far for-



1. Forward bias current-voltage characteristics for Cr, Pd, Rh, and Pt Schottky barriers on a-Si. Inset shows the series resistance limit for the Cr and Pt diodes.

ward bias currents for the Cr and Pt barriers formed on two different a-Si samples. The exponential region yields values of n between 1 and 1.2, values which were also obtained on the single crystal diodes. It is evident from Fig. 1 that the saturation current density, J_o (and the barrier height ϕ_B) depend on the metal. The far forward bias results shown in the inset for Cr and Pt indicate from Eq.(5) a built-in potential of 0.25 and 0.5 V, respectively. The series resistances of these two diodes are equal to within a factor of two, even though they were formed on two different a-Si samples, and correspond to a-Si resistivities of 7×10^6 and 1.3×10^7 Ω-cm.

The same values of V_o are obtained from capacitance measurements as a function of bias carried out at ac frequencies of 100 Hz. This is shown for the Cr and Pt diodes in Fig. 2.

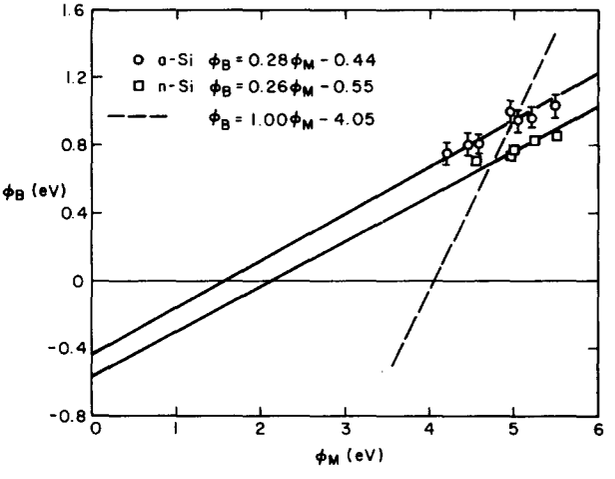


2. The $1/C^2$ vs V plots for the Cr, Pt diodes whose I-V characteristics are shown in Fig. 1. Also indicated in the figure are the values of V_o and the space charge densities in the barrier regions.

The good agreement between the values of V_o (for the same metals) obtained from the two measurements indicates a thin insulating nascent oxide, and the differences between the values of V_o for the different metals reflect the changes in ϕ_B arising from the metal work function. In addition to the above characteristics, measurements of the short-circuit currents and the open-circuit voltages as functions of illumination were in agreement with the usual diode equation and gave the same values of J_o as the dark I-V measurements.

The barrier heights can be determined using Eq.(4) as well as Eq.(2) providing E_f is known. The values of B used in Eq.(4) for these a-Si films were 3×10^6 A/cm^2 [1] and 2×10^7 A/cm^2 for the single crystal Si. The values of E_f used in Eq.(2) for the a-Si, obtained from the temperature dependence of the series resistance between 0°C and 100°C, were from 0.55 to 0.6 eV. The single crystal values of E_f were estimated from the resistivity of the wafers. Agreement within ~0.05 eV was obtained for the values of ϕ_B on a-Si using the two independent measurements and even better agreement was obtained with the single crystal Si. Furthermore, these a-Si values of ϕ_B are in good agreement with values obtained from the temperature dependence of the junction photovoltaic characteristics.[11]

The barrier heights, ϕ_B, measured for the different metal Schottky barriers on a-Si and single crystal Si are plotted as a function of the metal work function ϕ_M in Fig. 3. In Fig. 3 the form of Eq.(1) is indicated through the experimental points together with the dependence of the single crystal ϕ_B on ϕ_M in the absence of any surface state effects. Since there are large discrepancies the values quoted for the work functions of metals[12] no errors in ϕ_M are indicated; however, the effect of metal work functions on the two types of diodes can be directly compared. Although there is scatter in the data the results obtained with single crystal Si are similar to those reported in reference 6. Even though the a-Si barriers are consistently higher than those on single crystal Si there is a very similar trend in their dependence on ϕ_M. Substituting the values of C_1, indicated in Fig. 3, into Eq.(1) the densities of surface



3. The plot of ϕ_B for the a-Si and single crystal Si Schottky barriers vs metal work function ϕ_M. Also indicated in the figure are the values of C_1 and C_2 from Eq.(1) and the dependence of the single crystal ϕ_B in the absence of surface state effects.

states affecting the barrier heights are 3×10^{13} cm^{-2}eV^{-1} for δ = 5 Å and 1×10^{13}cm^{-2}eV^{-1} for δ = 15 Å (for ε_i equal to that of SiO_2). The values of C_2 reflect the differences in barrier heights on a-Si and single crystal Si and are related to the differences in the bandgap, electron affinity, and the position of the Fermi level at the surface prior to the formation of the metal contact. Because of the errors in the data, C_2 cannot accurately be extrapolated. However, from the experimentally obtained values of C_1 and C_2 a rough estimate can be made for the position of the Fermi level at the surface prior to the formation of the metal contact.[6] Using the crystalline silicon value for the electron affinity, this position is ~1.0 eV from the a-Si conduction band. This is in the neighborhood of two-thirds of the bandgap, the same fraction

estimated for crystalline Si.[6]

Although there are certain assumptions made regarding the dependence of ϕ_B on ϕ_M,[6] they apply to both types of Si. Consequently, the results presented reflect densities and energy distributions of surface states for both crystalline and amorphous silicon. These states in the case of a-Si can of course depend on the method of its fabrication. However, for the densities of $\sim 10^{13} cm^{-2} eV^{-1}$, just as in the case of single crystal Si, their effect cannot be entirely ignored in the interpretation of junction characteristics. In metal/thick insulator/a-Si structures the effect due to a charged surface state density of $10^{13} cm^{-2}$ is equivalent to a bulk a-Si space charge density of $10^{18} cm^{-3}$ extending over a thickness of 1000 Å. Furthermore, the pinning of the barrier height by these surface states results in junctions having barrier heights ≥ 0.7 eV on n-type discharge produced a-Si even with low work function metals such as Al and Cr. Consequently, unless techniques similar to those used in crystalline semiconductors are employed, ohmic contacts cannot be readily achieved in a-Si just by evaporation of low work function metals.

Acknowledgment - The authors would like to thank R. E. Daniel and A. R. Triano for their technical assistance; D. Hoffman and F. Tams for the metal evaporations; and B. F. Williams for helpful discussions.

REFERENCES

1. C. R. Wronski, D. E. Carlson, and R. E. Daniel, Applied Physics Letters 29, 602 (1976).

2. D. E. Carlson, C. R. Wronski, A. R. Triano, and R. E. Daniel, Proceedings of the 12th Photovoltaic Specialists Conference, Baton Rouge, Louisiana, November 15-18, 1976. (to be published)

3. C. R. Wronski, D. E. Carlson, R. E. Daniel, and A. R. Triano, Technical Digest, IEEE International Electron Devices Meeting, Washington, D.C., December 6-8, 1976, p.75.

4. See, for example, N. F. Mott and E. A. Davis, Electronic Processes in Noncrystalline Materials (Clarendon Press, Oxford, England, 1971).

5. A. Maden, P. G. LeComber, and W. E. Spear, Journal of Noncrystalline Solids 20, 239 (1976).

6. A. M. Cowley and S. M. Sze, Journal of Applied Physics 36, 3212 (1965).

7. S. M. Sze, Physics of Semiconductor Devices (Wiley-Interscience, New York, 1963).

8. J. Schewchun, M. A. Green, and F. D. Ring, Solid State Electronics 17, 563 (1974).

9. A. M. Goodman, Surface Science 1, 5 (1964).

10. A. M. Cowley, Journal of Applied Physics 37, 3024 (1966).

11. To be published.

12. A. M. Sommer, Photoemissive Materials (John Wiley and Sons, New York, 1968), p.21.