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Short Communication

The Influence of Surface Preparation on Rectification in Aluminum–Polycrystalline Silicon Solar Cells

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An experimental study is presented of aluminum–polycrystalline silicon contacts concerned with the dependence of the Schottky barrier characteristics ϕ_b and n (barrier height and exponential ideality factor) on the chemical preparation of the polycrystalline silicon surface prior to the aluminum evaporation. It is observed that an etching time of $\simeq$ 3 min in HNO_3:HF:CH_3COOH in the proportions 3/1/1 is optimum, for which case $\phi_b \simeq$ 0.85 - 0.9 V and $n \simeq$ 1.1 - 1.2 in the resultant devices. This work has implications for the optimization of MIS–Schottky barrier polycrystalline silicon solar cells.

The purpose of this communication is to show, in quantitative terms, the dependence of the electrical behaviour of aluminum–*p* type polycrystalline silicon Schottky barrier junctions on the chemical preparation of the polycrystalline silicon surface prior to metal evaporation. Our interest in this metal–semiconductor contact stems from its promise as the photovoltaic junction in polycrystalline silicon solar cells [1 - 4].

The material with which we are concerned in this study is *p*-type cast polycrystalline silicon wafers of the 'Silso' type, as obtained from Wacker Siltronic Corp. This material is initially cleaned in a series of organic solvents (trichloroethylene, acetone, methanol) and then in deionized water, using an ultrasonic cleaner. We have then subjected the wafers to a chemical etching procedure at 300 K in a mixture of acids (HNO_3:HF:CH_3COOH in the proportions 3/1/1). During the etching process the solution is continually agitated, and to terminate this process the solution is flooded with deionized water.

The current–voltage characteristics of the aluminum–polycrystalline silicon contacts were found to be very sensitive to the etching time, demonstrating poor rectification properties for both very short and very long etching times. The optimum characteristics were obtained for an etching time of ≃ 3 min, and under these conditions the characteristics corresponded to a near-ideal Schottky barrier with a current–voltage characteristic

$$I = a A^*T^2 \exp\left(-\frac{\phi_b}{V_T}\right)\left[\exp\left(\frac{V}{nV_T}\right)-1\right] \tag{1}$$

where a is the area of the contact (0.03 cm^2), A^* is the modified Richardson constant for the thermionic emission of holes into the metal (30 A cm^{-2} K^{-2}), $V_T = KT/q$, ϕ_b is the Schottky barrier height, and n is a measure of the ideality of the rectification characteristics ($n > 1$). V in eqn. (1) is positive for a positive voltage on the polycrystalline silicon with respect to the metal.

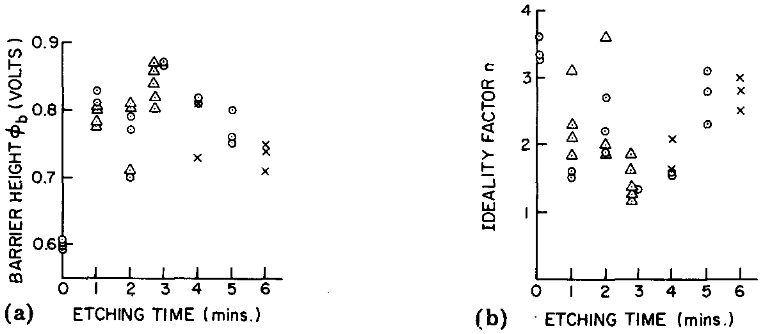

Fig. 1. Dependence of (a) Schottky barrier height, ϕ_b, and (b) n-value or ideality factor of aluminum–p-type polycrystalline silicon contacts upon etching time in 3/1/1 HNO_3:HF:CH_3COOH. The symbols ⊙, △, and × refer to different batches of devices (processed independently).

The current–voltage characteristics of the aluminum-p type polycrystalline silicon contacts were measured as a function of etching time, and the values of ϕ_b and n for the best fit to eqn. (1) were obtained in each case. The results are shown in Fig. 1, from which the limits on the reproducibility may also be determined. In the best case (an etching time of ≃ 3 min), it was observed that ϕ_b ≃ 0.87 V and n ≃ 1.1 - 1.2. The observed barrier height values are consistent with the presence of an interfacial oxide layer of ≃ 15 Å thickness, as expected from the polycrystalline silicon surface treatments [1, 5]. We believe that the mechanism resulting in $n > 1$ for the near-ideal devices is primarily recombination current in the space-charge region, which provides an $\exp(V/2V_T)$ contribution in parallel with the $\exp(V/V_T)$ dependence of the thermionic emission current. This recombination is thought to occur principally at the grain boundaries in the polycrystalline silicon [4]. The reported ϕ_b's are only a lower limit for those cases in which $n > 1$, since the presence of a recombination current component gives an apparent saturation current which is larger than that due to the thermionic emission alone. From optical measurements we have determined that $\phi_b > 0.9$ V in some cases.) The n values greater than two are presently unexplained.

They may result from voltages developed across interfacial oxide layers due to dipole effects [5] associated with large densities of polycrystalline silicon–oxide interface states or they may be due to the product of a complex polycrystalline silicon surface structure.

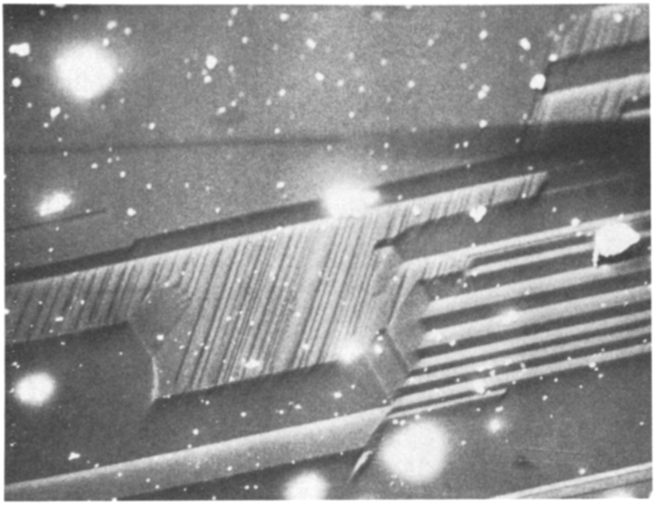

Fig. 2. Surface structure of polycrystalline silicon following etching process of Fig. 1 for $t \simeq 6$ min, as obtained by scanning electron microscopy. Bright spots are an artifact of the microscopy. Dimensions of the photograph correspond to 350 μm × 250 μm on sample surface.

On this latter point, Fig. 2 shows a scanning electron micrograph of the polycrystalline silicon surface after etching for $\simeq$ 6 min. The complex relief structure is indicative of a non-uniform etch rate associated with a preferential attack on the grain boundaries, and an orientation dependence of the etch rates on the surface of the grains. The closely-spaced parallel lines across the central grain in Fig. 2 are attributed to a dislocation structure which is produced in this grain as a result of bidirectional stress imposed by the adjacent grains. This result implies that the minority carrier lifetime within the grains themselves (away from the grain boundaries) of this material may be considerably smaller than that found in crystalline silicon as a result of recombination at these dislocations.

Finally, we wish to point out an ageing mechanism that we have observed for aluminum–polycrystalline silicon contacts. The severity and the rapidity of this ageing process increase with reduction in the aluminum thickness. For an aluminum thickness of $\simeq$ 100 Å or below, such as would be required in photovoltaic applications, the characteristics degrade in a matter of hours (ϕ_b decreases and n increases), whereas for much thicker aluminum layers, the ageing is greatly retarded or eliminated. We attribute these ageing phenomena to the mechanism of Ponpon and Siffert [6], that oxygen permeates the metal film and produces an interfacial oxide layer at the metal–

semiconductor interface. In this connection, the work of Lillington and Townsend [1] on aluminum–polycrystalline silicon solar cells is encouraging, since they report no appreciable instability, even with very thin aluminum layers, provided that an anti-reflection coating of ZnS is present. Such a coating is obviously serving also as a barrier against chemical attack.

In summary, if one is attempting to reduce the dark currents in rectifying aluminum–polycrystalline silicon contacts (for example, in order to increase the open-circuit voltage of a photovoltaic cell based upon this junction), an etching time of 3 min in 3/1/1 HNO_3:HF:CH_3COOH is optimum, in which case $\phi_b \simeq 0.85 - 0.9$ V and $n \simeq 1.1 - 1.2$. This results in a dark current of $\simeq 10^{-6}$ mA cm^{-2}, and for an aluminum–polycrystalline silicon photovoltaic cell with a short-circuit current density of 25 mA cm^{-2}, in an open circuit voltage of $\simeq 0.42$ V, in the absence of improvements from an interfacial layer [1].

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