Amorphous-silicon m.i.s. solar cells

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Indexing terms: Metal-insulator-semiconductor devices, Solar cells

Abstract: M.I.S. solar cells of amorphous silicon on stainless steel, with a top barrier contact of Ni/TiO_x, have given 4·8% power conversion efficiency without an antireflection coating. The insulating layer, with an optimum thickness of ≈ 2 nm, compensates for the low work function of nickel compared with platinum, and enables similar high open-circuit voltages (up to 680 mV) to be obtained. The fill factor is not appreciably degraded by the addition of an insulating layer, unless this is thicker than ≈ 3 nm. Under illumination, the diode characteristics change compared with their behaviour in the dark; the diode factor, the barrier height, and the series resistance are all dependent on light intensity.

1 Introduction

In 1975 Spear and Le Comber demonstrated that amorphous-silicon films prepared by the r.f. glow-discharge decomposition of silane could be doped by the addition of phosphine or diborane to the gas, thus controlling the electrical conductivity over ten orders of magnitude.[1,2] Since then there has been renewed interest in using silicon thin films for cheap solar cells. We have investigated metal-amorphous-silicon cells rather than *p-n* or *p-i-n* structures, and here show that even at this early stage in their development the power conversion efficiency is rapidly approaching the 8% thought to be the minimum acceptable value for large-scale terrestial use. Only RCA in the USA have reported comparable efficiencies with amorphous silicon (2·4% for *p-i-n* cells,[3,4] and up to 5·5% for platinum Schottky-barrier cells[4,5]). Their cells were of small area (up to 2×10^{-2} cm^2) and were antireflection coated. We have achieved efficiencies of up to 4·8% in 60 mW cm^{-2} simulated sunlight for m.i.s. cells, of area up to 7×10^{-2} cm^2, with a cheaper nickel/TiO_x contact and no antireflection coating. The insulating layer between barrier metal and semiconductor compensates for the low work function of Ni compared with Pt, enabling similar open-circuit voltages to be obtained.

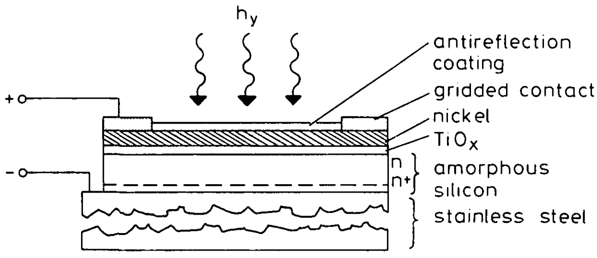

Fig. 1 *Cross-sectional view of a complete amorphous-silicon m.i.s. solar cell*

2 Device fabrication

The amorphous-silicon films used in this study were deposited on stainless-steel substrates by the glow-discharge technique at Dundee University. A thin n^+ layer was deposited first, to ensure a good ohmic contact between the substrate and the subsequent $\approx 1\,\mu$m of undoped, high-resistivity silicon.

Paper T156 S, received 30th November 1977

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Semitransparent barrier contacts were deposited on the top surface by vacuum evaporation in an oil-free stainless-steel chamber, using a mask/substrate changer to allow first TiO_x (1–3 nm) and secondly nickel (≈ 6 nm) films to be produced during the same evacuation cycle (Fig. 1). Growth of the layers was measured by a quartz-crystal deposit-thickness monitor. Several metal contacts of area up to 7×10^{-2} cm^2 were used for each sample oxide thickness, with no antireflection coating or encapsulation. Contact was made to these semitransparent films with a Research Instruments Ltd. probe unit.

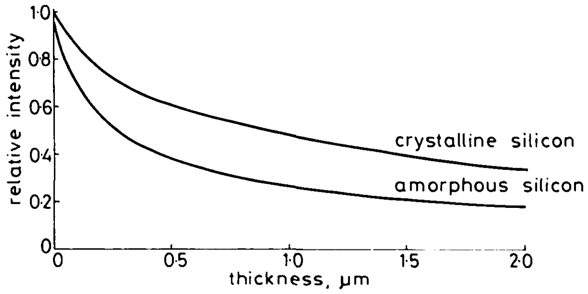

Fig. 2 *Attentuation of a.m.1 illumination through crystalline and amorphous silicon films, as a function of thickness*

Absorption coefficients were taken from References 6 and 7

3 Device characteristics

From reflectance data we have calculated the spectral absorption coefficient α of undoped amorphous-silicon films grown by the discharge technique at Heriot-Watt, and find that, depending on the growth conditions, α is at least ten times greater for amorphous silicon than for crystalline silicon, in agreement with other reported results.[3,6] It is apparent that a thin film of *amorphous* silicon should have the same absorptance as a thick film of *crystalline* silicon, for the spectral band which both absorb. Fig. 2 shows that the larger band gap of amorphous silicon does not detract from its effectiveness as an absorber of solar radiation. This graph indicates that Schottky-barrier cells, with their built-in field at the surface, should have an advantage for the collection of photogenerated carriers over *p-n* cells, with their deeper junction field. This may be especially important for amorphous silicon with its short minority-carrier lifetime; very few carriers generated outside the field region will reach the junction before recombination occurs.

The open-circuit-voltage spectral response of a typical amorphous silicon cell with a nickel barrier contact is

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shown in Fig. 3. This is typical of all the cells we have examined, using doped or undoped amorphous silicon, and with various top-surface barrier contacts.

From the illuminated current/voltage (I/V) characteristic of Fig. 4 it is evident that efficient cells can be made with the structure. The cell with this response has an efficiency of 2·6% in 43 mW cm^{-2} sunlight, increasing to 4·8% in 60 mW cm^{-2}. This increase in efficiency is partially due to the decrease in effective series resistance of the cell with increase in illumination intensity. In the dark, the series resistance of the diodes indicates an amorphous-silicon resistivity of $\approx 1{\cdot}7 \times 10^5\ \Omega$ cm, which is reduced to $\approx 2{\cdot}7 \times 10^4\ \Omega$ cm when irradiated with 60 mW cm^{-2} illumination; consequently, the dark and illuminated I/V curves cross over, in a similar manner as for Cu_xS/CdS cells. This photoconductive effect means that the advantage of a wider field region in *un*doped material is not offset by the higher bulk series resistance.

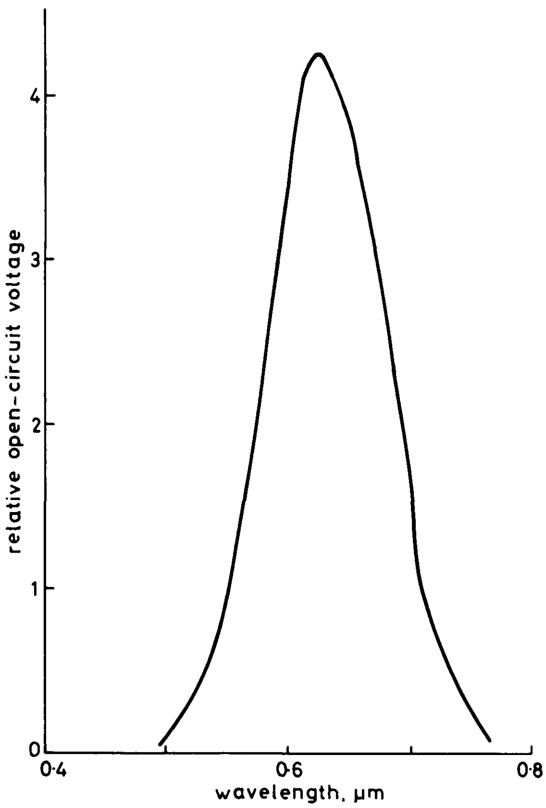

Fig. 3 *Spectral response of the open-circuit voltage for a typical amorphous-silicon Schottky-type cell (uncorrected for monochromator response)*

There is an accompanying decrease in the diode factor n (eqn. 1) when the device is illuminated. In the dark, the diodes with a thin interfacial oxide layer have an n value greater than 3, but under weak illumination this falls to 2, and approaches 1·2 with higher-intensity illumination. The junction barrier height is also increased by illumination. An increase for a typical m.i.s. diode is from 0·78 eV in the dark to 0·91 eV under solar-radiation intensities. These values were determined as follows.

The illuminated I/V characteristics are given by

$$I = I_0 \left\{ \exp \frac{e}{nkT}(V - IR_s) - 1 \right\} - I_L - \left(\frac{V - IR_s}{R_{sh}} \right) \qquad (1)$$

where I_0 is the saturation current, R_s the series resistance, R_{sh} the shunt resistance and I_L the light-generated current. For the values of series and shunt resistance found in our cells, the light-generated current is numerically equal to the short-circuit current I_{sc}. This in turn is proportional to the illumination intensity for the range of interest to solar cells (Fig. 5), with a proportionality constant of 0·13 for the units used on the graph. As a result, the open-circuit voltage V_{oc} should be proportional to the log of the light intensity (see eqn. 2), which is confirmed by Fig. 6, for the range of interest.

$$V_{oc} = \frac{nkT}{e} \ln \left(\frac{I_{sc}}{I_0} \right), \quad I_{sc} \gg I_0 \qquad (2)$$

A plot of log J_{sc} (the short-circuit current density) against V_{oc} should therefore be linear, with a slope giving the value of the illuminated-diode factor. Fig. 7 shows this plot for the same Ni/TiO_x diode used for Figs. 3, 4 and 5, giving the n values quoted previously. The height of the barrier at the illuminated junction is found from I_o, the intercept in Fig. 7, which is confirmed by the value found from the intercept of Fig. 6 (using the proportionality constant to convert light intensity into short-circuit current). Using eqn. 3, the barrier height is calculated, assuming thermionic-emission theory rather than diffusion theory (which *is* more appropriate to low-mobility semiconductors[8]), since there are fewer assumptions to be made in assigning values to the parameters, and since the same numerical result is obtained from both methods.

$$I_o = A^* T^2 \exp \left(\frac{-e\phi_{Bn}}{kT} \right) \qquad (3)$$

where the constant A^* is assumed to be 100 A cm^{-2} (the value for crystalline n-Si).

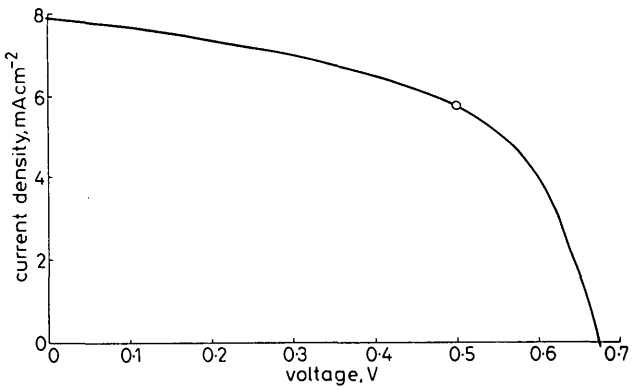

Fig. 4 *Current/voltage characteristic of a typical Ni/TiO_x contacted cell, illuminated with 60 mW cm^{-2} simulated sunlight*

Efficiency at the indicated maximum power point is 4·8% with a fill factor of 0·51

4 The insulating layer

In the previous Section we have confined our remarks to features of the m.i.s. cells that are common to all, irrespective of the interfacial layer thickness δ. In fact, the values of both V_{oc} and J_{sc} are strongly dependent on δ. Fig. 8 illustrates this dependence, and shows an optimum value for δ of $\approx$ 2 nm. When these values are combined with the fill factor, which changes only gradually with δ over this range, there is a similar peak in the resultant power conversion efficiency Fig. 9. These results were obtained from the same amorphous-silicon film, and similar behaviour has been observed for other samples. M.I.S. cells on crystalline silicon have shown a similar dependence of efficiency on the insulating layer thickness.[9–12]

The degradation in fill factor when an insulating layer slightly thicker than $\approx 2\,nm$ is added is mainly due to a poor illuminated shunt resistance, rather than to an increase in series resistance. Methods of cell fabrication that avoid this limitation are under investigation, and a fuller discussion will be reported elsewhere.

We have observed no degradation of the high open-circuit voltages of these cells (up to 680 mV in weak sunlight), even after unprotected storage in air. The addition of an insulating layer does not appear to introduce any instability in performance.

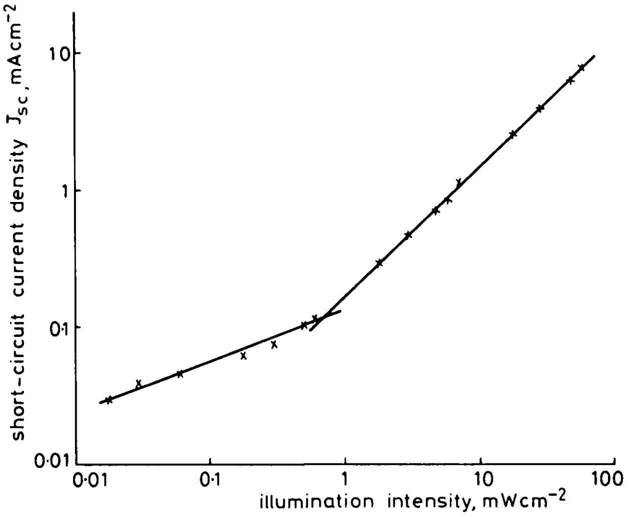

Fig. 5 *Short-circuit current density for a typical Ni/TiO$_x$ contacted cell, as a function of white-light intensity*

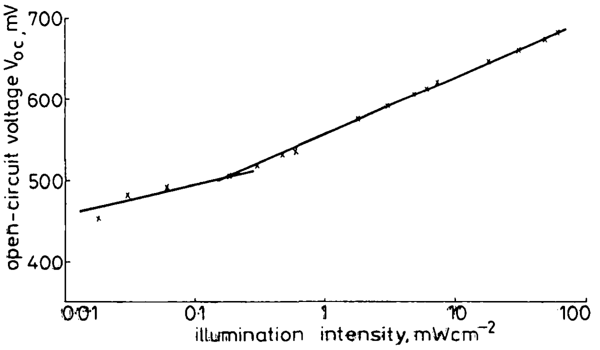

Fig. 6 *Open-circuit voltage for a typical Ni/TiO$_x$ contacted cell, as a function of white-light intensity*

5 Discussion

The effect of the insulating layer is to compensate for the low work function of nickel in comparison with Pt, Pd or Ir, giving similar effective barrier heights at the junction. Although a high-work-function metal *is* essential for obtaining the highest barriers in a true Schottky diode on amorphous silicon,[13–15] the economic advantages of a cheaper more easily deposited metal may be realised by an m.i.s. diode with a tailored interfacial region. The theory of m.i.s. diodes has been extensively reported,[16,17] together with specific treatment of photovoltaic diodes.[18–24] These calculations for crystalline semiconductors appear to be equally valid for glow-discharge amorphous silicon.

The principal influence of the insulating layer is the reduction of the *majority*-carrier flow from the semiconductor without an accompanying reduction of the desired *minority*-carrier flow. Further influence is exerted by the interface states, within the bandgap, at the junction. Whether or not these are in equilibrium with the metal, the conduction band electrons or the valence band holes, determines the maximum advantage to be gained by the addition of an interfacial layer to a chosen metal-semiconductor couple. Whereas the *width* of the insulating layer is important for the degree of suppression or tolerance of the various tunnelling-current components across it, it is also possible to have a different barrier *height* for electrons and holes, depending on the electron affinity differencc between semiconductor and insulator. The importance of this parameter in diode behaviour means that bulk values of the insulator constants should not be applied for such narrow layers, and it is difficult at present to determine which m.i.s. model applies to our cells. For *all* models there is a peaked dependence of cell efficiency with insulator thickness.

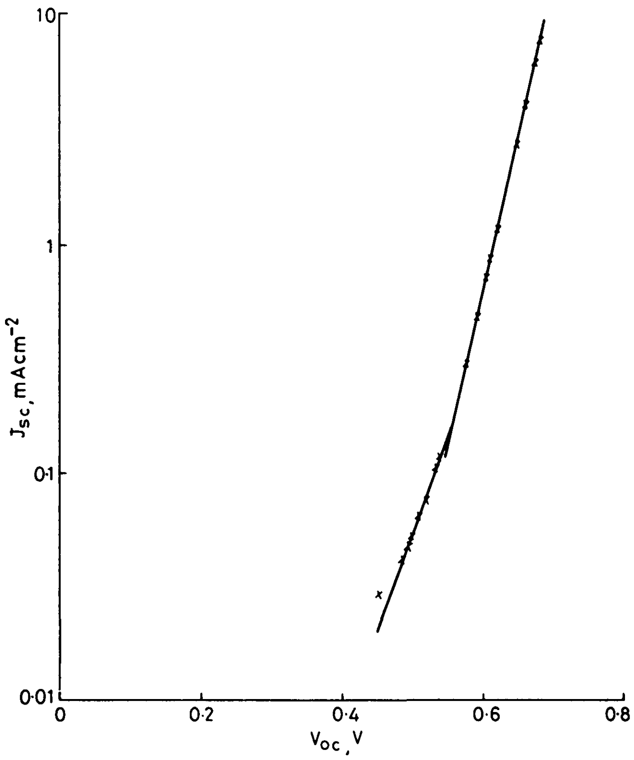

Fig. 7 *Short-circuit current density against open-circuit voltage for the cell of Figs. 3–5*

In many respects our cells have the same features as those of RCA, indicating that it is the amorphous silicon rather than the junction itself which is limiting present performance. The increase in junction capacitance on illumination observed by Wronski[25] is seen in our diodes as well, and is due to the decrease in the depletion-region width. Although this might be expected to lead to collection efficiency worsening with increase in illumination intensity, we have already seen that the cells discussed here have an improving performance with increase in intensity. Coupled with this is the observation that n decreases from ≈ 2 in weak illumination to $\approx 1{\cdot}2$ in sunlight intensities. Taken together, these features suggest that the increased field in the depletion region, as the intensity is increased, reduces the number of carriers lost by recombination. Any further increase in cell efficiency must depend either on increasing the carrier-collection efficiency outside the field region, or on producing a field which extends across the whole device.

6 Conclusion

The power conversion efficiency of 4·8% reported here may be increased by adding an antireflection coating to the top metal surface, but the present contact transmittance of $\approx 50\%$ can only be increased to $\approx 70\%$ since the limit on passing light into the silicon is set by reflections from the metal-silicon interface. This would imply that an efficiency of $\approx 6{\cdot}3\%$ is attainable with our present optimised Ni/TiO_x (2 nm) contacts. A closer approach to the minimum required efficiency of 8% necessitates an increase in the minority-carrier lifetime of amorphous silicon, so that photogenerated carriers can be collected by the junction from outside the field region. If the high open-circuit voltages reported here were retained, and the fill factor were to be increased to a not unreasonable 0·7, then an 8% efficient cell would have to produce an a.m.1 short-circuit current density of $\approx 17\,mA\,cm^{-2}$, only slightly greater than the $15\,mA\,cm^{-2}$ suggested by Debney[26] from present-day amorphous-silicon transport properties. Still higher voltages should be reached by using the tailored m.i.s. structure with a high work-function metal.

7 Acknowledgments

We are grateful to W.E. Spear and P.G. Le Comber of Dundee University for their co-operation in this project, and to Stewart Kinmond for preparing amorphous films. The work was begun with a grant from the Wolfson Foundation, and is now supported by the Science Research Council, UK.

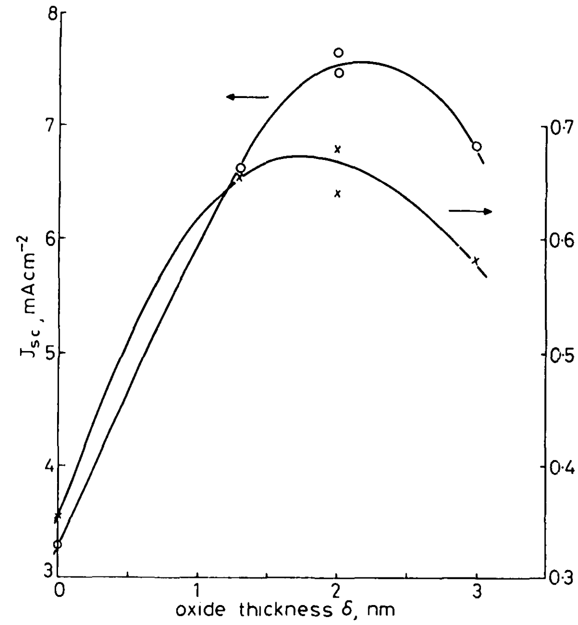

Fig. 8 *Dependence of open-circuit voltage and short-circuit current density on interfacial-oxide thickness (in $\approx 60\,mW\,cm^{-2}$ simulated sunlight)*

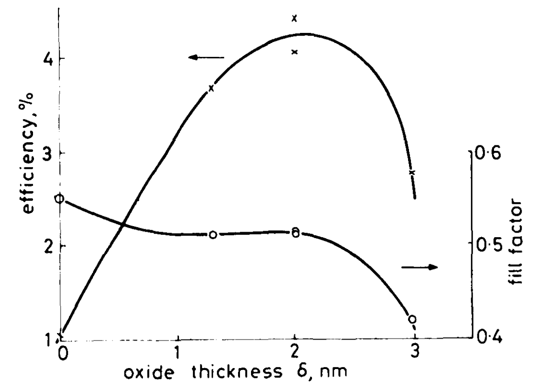

Fig. 9 *Dependence of fill factor and power conversion efficiency on interfacial-oxide thickness (in $\approx 60\,mW\,cm^{-2}$ simulated sunlight)*

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