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Characterization of a-Si:H thin films prepared by dc glow discharge of silane

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Abstract. A dc glow discharge apparatus for preparing amorphous silicon films from silane gas is described. The films are characterized by electron microscopy, infrared spectroscopy, electrical conductivity and photoconductivity. The deposition parameters which give good photoconducting films are established. The Staebler-Wronski effect is studied and is found to be smaller in vacuum than in air. A photovoltage is observed in structures with gold as the Schottky-barrier metal. The conversion efficiency of the device is about 1%. The results are compared with those in the literature, and the improvements which might result in a better conversion efficiency are pointed out.

Keywords. Characterization; glow discharge; amorphous silicon; thin film; silane.

1. Introduction

Thin films of a-Si:H prepared under suitable conditions by the glow discharge of silane (SiH_4) are found to have desirable electrical and optical properties. These films can be doped *n*-type or *p*-type because they have lesser number of localized states in the mobility gap as compared to a-Si prepared by other methods (Spear and Le Comber 1975). This reduction in the number of localized states is attributed to the presence of hydrogen in the lattice (Brodsky *et al* 1977), which compensates the dangling bonds. But the amount of hydrogen in the lattice is about 10-35 at. % which is $\sim$100 times more than the dangling bonds observed in the case of evaporated a-Si. Thus it is believed (Fritzsche *et al* 1978) that it is not only the compensation of dangling bonds but also the modification of the structure because of the presence of hydrogen which is responsible for the interesting properties of a-Si:H.

We report the design of a dc glow discharge apparatus fabricated in our laboratory. The structural characterization of a-Si:H by electron microscopy and IR spectroscopy is also reported. The IR spectra shows the presence of hydrogen in our films. Electrical characterization of the samples is done by studying the dark conductivity and photoconductivity as a function of temperature. A photovoltage (V_{oc}) $\approx$350 mV is observed in sandwich structures of NiCr/a-Si:H/Au (top), upon shining white light (flux = 5×10^{14} photons/cm^2/sec). After exposing to AM1 light for about 4 hr the room temperature conductivity decreases. This effect is found to be more in air than in vacuum by about an

order of magnitude. In both the cases, however, the magnitude of the change in room temperature conductivity upon exposing to light is much smaller in our films than reported in the literature (Staebler and Wronski 1977). The results are presented in § 2·3c. Finally, these results are discussed in § 3.

2. Experimental

2·1 *Details of the glow discharge apparatus*

A mixture 3% silane and 97% argon is subjected to a dc electric field in a glow discharge reaction chamber of pyrex glass shown in figure 1. A capacitor geometry is used for the discharge. The diameter and length of the reaction chamber are 16 and 20 cm respectively. An aluminium plate of 10 cm diameter is used as anode and an aluminium screen as cathode. The screen is used to overcome the difficulties associated with the charging of glass substrates during the discharge. The substrates are kept about 1 cm away from the screen on another stainless steel plate which contains a heater and can be heated up to 500°C.

Since silane is highly reactive the gas mixture is first filled in an auxiliary cylinder at a pressure of about $3\text{–}6 \times 10^3$ kg/m^2, to minimize the danger. The mixture is let into the reaction chamber through a needle valve which controls the flow. The system is constantly pumped by a rotary pump and a pressure of about 1 torr is maintained during the discharge. The gases coming out of the reaction chamber are passed through an oven kept at $\approx$1000°C to thermally decompose any silane which might escape the electric field. A magnetic isolation-cum-air-admittance valve is placed between the oven and the rotary pump and is connected in such a way that during an emergency, such as, a sudden power failure, the pump is isolated and the system is flooded with dry nitrogen

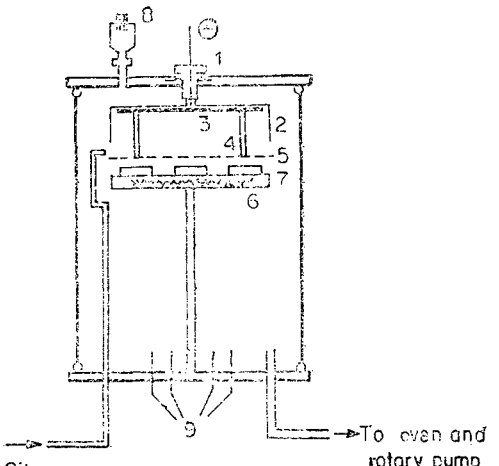

Figure 1. Glow discharge reaction chamber. **1.** High tension feed through, **2.** Pyrex anode shield, **3.** Anode, **4.** Ceramic post, **5.** Aluminium screen (Cathode), **6.** Steel plate containing heater, **7.** Substrates, **8.** Thermocouple gauge, **9.** Electrical feed through.

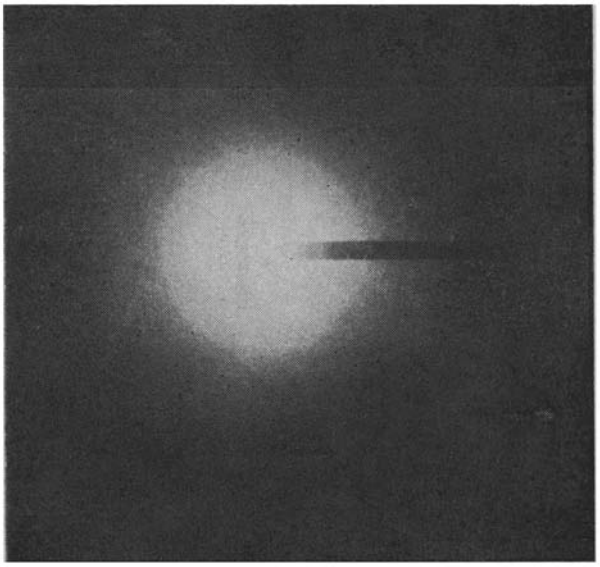

Figure 2. Electron diffraction micrograph of a-Si:H (T_S = 580 K).

gas. Before starting the discharge the system is evacuated to 10^{-2} torr and baked at 200°C for 12 hr. Typical deposition parameters which result in good quality films are listed below:

Substrate temperature = 580 K, pressure = 1 torr; distance between anode and the screen=2·5 cm; DC voltage=460 V: discharge current=6·3 mA; power density = 40 mW/cm²; Deposition rate = 1 Å/sec.

2·2 *Structural characterization*

2·2a *Electron microscopy*: Copper or tungsten electron microscopic grids coated with carbon are used for deposition of amorphous silicon films of about 500 Å thickness for transmission electron microscopy. An electron diffraction micrograph of one such sample deposited at 580 K is shown in figure 2. It consists of diffused rings, which shows the amorphous nature of the films.

2·2b *IR spectroscopy*: a-Si:H samples of about 5000 Å thickness are prepared on KBr pellets. Figure 3 shows the transmittance from 200 to 2500 cm^{-1} wavenumber, recorded on a Perkin Elmer 580 spectrophotometer. Curve *a* is for a sample prepared at 300 K whereas curve *b* is for samples prepared at 580 K. Samples deposited at 300 K have IR peaks at 2080, 1000, 890, 850 and 635 cm^{-1}. In samples deposited at 580 K, IR peaks at 1000, 890 and 850 cm^{-1} are absent and a new peak appears at 2000 cm^{-1}. The identification of these peaks is also given in figure 3. These results agree with the literature (Lucovsky *et al* 1979).

2·3 *Measurements and results*

All the samples are heat-dried at 200°C for 2 hr in a vacuum of 2×10^{-5} torr before doing any electrical measurements.

2·3a *Conductivity*: dc conductivity (σ) measurements are done on samples on Corning 7059 glass substrates having chrome gold or nichrome contacts above or below the a-Si:H film in a coplanar configuration with a gap-spacing varying between 0·4 mm to 1cm. σ is found to be independent of these parameters. Figure 4 shows $\sigma(T)$ of a-Si:H prepared at substrate temperatures (T_s) = 300, 450 and 580 K. $\sigma(T)$ for an evaporated Si sample is also shown for comparison. Films prepared at 300 and 580 K have similar σ at 300 K $\sigma(300\text{ K}) = 10^{-8}$ ohm^{-1} cm^{-1}, and have activation energies (ΔE) = 0·62 e_A and 0·7 eV respectively whereas the samples prepared at 450 K have σ (300 K) = 4×10^{-10} ohm^{-1} cm^{-1} and ΔE = 1 eV. These results are in qualitative agreement with the literature (Le Comber *et al* 1972).

2·3b *Photoconductivity*: Films deposited at 300 K are not photoconducting. The photoconductivity (σ_{ph}) for films with T_s = 450 K is 5×10^{-6} ohm^{-1} cm^{-1} and 10^{-4} $ohm^{-1}cm^{-1}$ for T_s = 580 K for white light of 5×10^{14} photons/cm²/sec. The results of variation of photoconductivity as a function of temperature in the range 300 K $\geq T \geq$ 200 K are shown in figure 5 for a sample prepared at 580 K. The results of Wronski and Carlson (1977) are also shown for comparison.

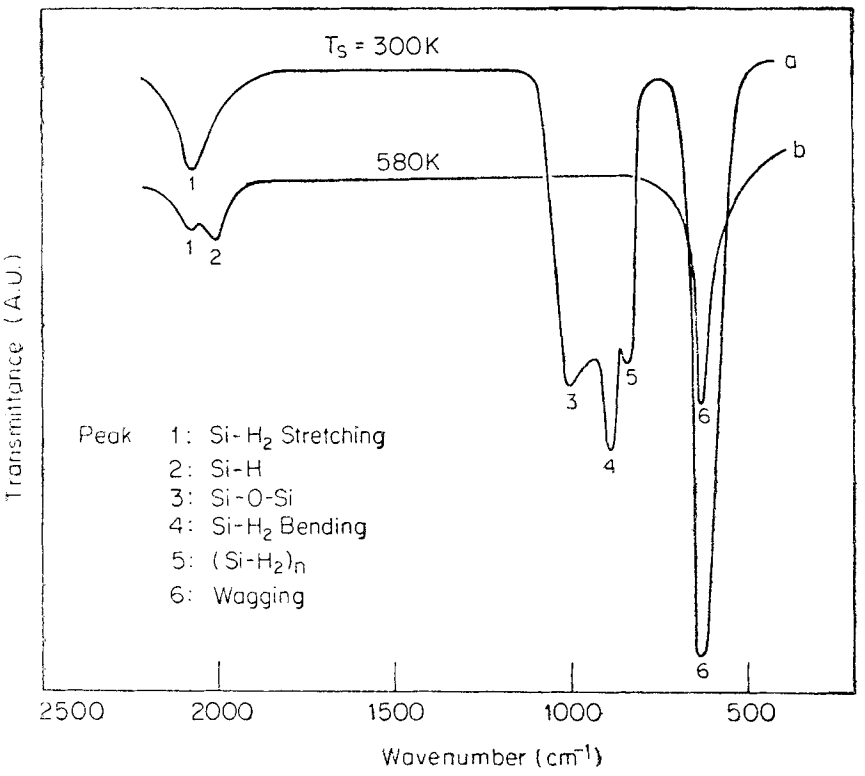

Figure 3. IR spectra of a-Si : H.

2·3c *Staebler-Wronski effect*: Staebler and Wronski (1977) found that when samples of a-Si:H are exposed to AM1 light for about 4 hr at 300 K in vacuum, σ (300 K) of the samples reduces by about 4 orders of magnitude. We have looked for this effect in our films (T_s = 580 K) in air and as well as in vacuum. Figure 6 shows the results. Immediately after heat drying but before the light exposure the sample is in high conducting state with conductance (G) at 300 K = 7·5 x 10^{-11} ohm^{-1} and ΔE = 0·62 eV. After exposure to AM1 light for 4 hr in air it gets transformed to a low conducting state with G = 4·8 x 10^{-12} ohm^{-1} and ΔE= 1 eV. Upon annealing to 175°C in vacuum the sample returns to its high conducting state The sample is then exposed to light (with the same intensity) in a vacuum of 2 x 10^{-5} torr. Now G changes from 7·5 x 10^{-11} ohm^{-1} to 2·4 x 10^{-11} ohm^{-1} and ΔE from 0·62 eV to 0·7 eV. Thus we find that when our samples are exposed to light in vacuum, the effect is smaller. Further, in both cases the change in G is much smaller for our films than reported by Staebler and Wronski (1977).

2·3d *Photovoltaic effect*: We have observed a photovoltaic effect in a-Si:H films having a sandwich structure. The bottom electrode is of nichrome of thickness 1 μm. The top electrode, through which the light is shone, is of gold of thickness $\approx$ 100Å. The thickness of a-Si:H film is 1 μm. The typical area of such a

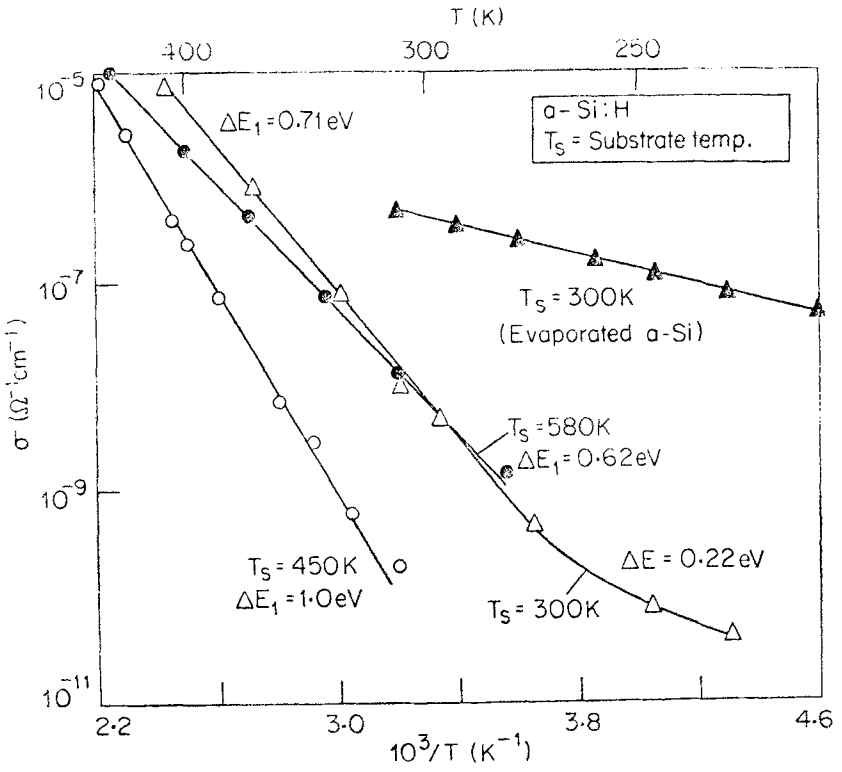

Figure 4. Variation of conductivity with temperature of a-Si:H.

device is 10^{-2} cm^2. Typically, open circuit photovoltage (V_{oc}) of a few hundred millivolts is obtained upon shining white light of photon flux 5 x 10^{14} photons/cm^2/sec. The short circuit current density is 1–3 mA/cm^2. The load characteristic of one such photovoltaic cell is shown in figure 7. The fill factor is about 0·35 and the calculated conversion efficiency (η) is about 1%.

3. Discussion

IR spectra deposited at 300 K have absorption peaks which correspond to Si-H_2 (stretching), Si-O-Si, Si-H_2 (bending), (Si-H_2)$_n$ polymer chains, and Si-H, Si-H_2, Si-H_3 (wagging) modes as shown in figure 3. In the sample deposited at 580 K the peak at 2000 cm^{-1} corresponds to Si-H (stretching). Thus it is clear that in films prepared at 580 K hydrogen is present mostly as monohydride. Also, the intensity of IR peaks is reduced in the sample deposited at 580 K. This shows that hydrogen concentration in samples deposited at 580 K is lower than the ones deposited at room temperature, in agreement with the published work (Lucovsky *et al* 1979).

Figure 4 shows that σ is thermally activated with two activation energies for the film prepared at 300 K. These might arise from two conduction mechanisms. In the temperature range 420K–300 K the band to band conduction seems

to dominate in which case ΔE is large (0·7 eV) whereas conduction in the extended band tails can explain the low ΔE (0·3 eV) in the temperature range 300 K to 230 K. The samples prepared at higher substrate temperature have a single activation energy, corresponding to band conduction.

Samples prepared at high T_S are found to be highly photoconducting. In these samples IR spectroscopy shows that hydrogen is present mostly as monohydrides. Since the conduction in the band tails is absent in these films, we might argue that the presence of monohydrides gives films having a lesser number of gap states resulting in the high photoconductivity; although the exact role played by such bonds is still far from clear. The thermoelectric power measurements on our samples (Shailendra Kumar 1981) show that our samples are *n*-type. The $\sigma_{ph}(T)$ curve agrees qualitatively with that obtained on undoped films by Wronski and Carlson (1977) (see figure 5) whose films are also of *n*-type. The activation energy of the low T part of the plot of σ_{ph} (T) can be used to estimate the depth of recombination centres. In our samples it is about 0·4 eV below the conduction band. This should be compared with 0·25 eV obtained by Wronski and Carlson (1977).

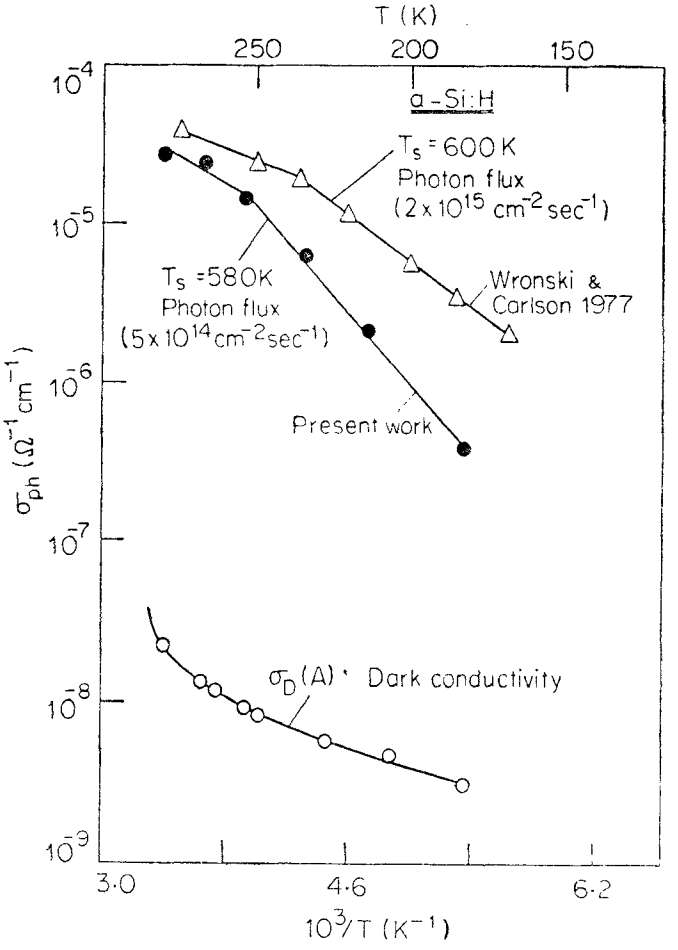

Figure 5. Variation of photoconductivity with temperature of a-Si:H

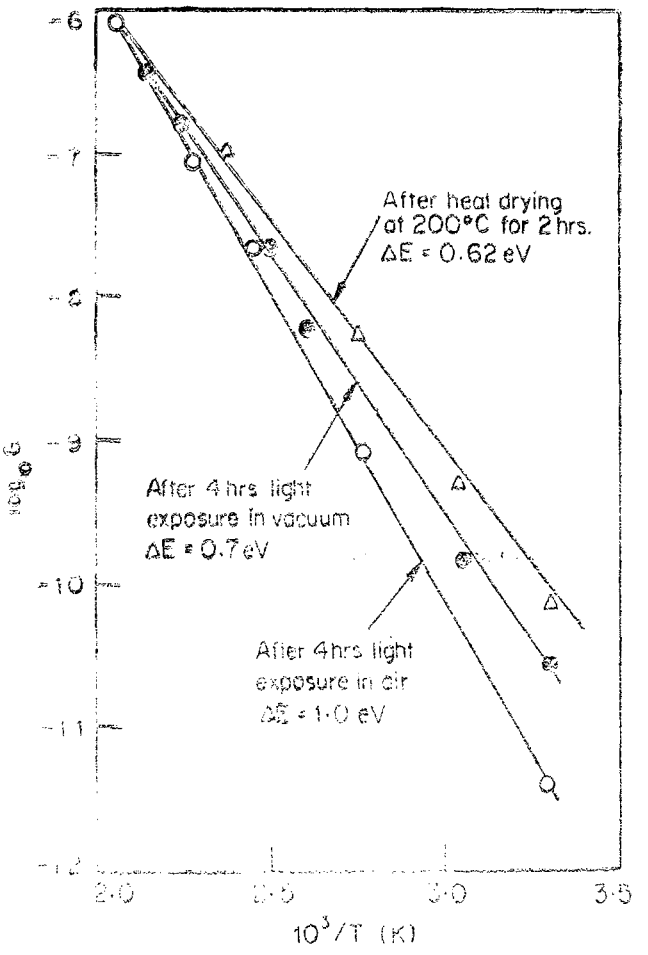

Figure 6. Staebler–Wronski effect in a-Si:H.

Three mechanisms have been proposed (Staebler and Wronski 1977) to explain the light-induced effects in a-Si films: (i) Existence of band bending at the film substrate interface, (ii) existence of band bending at film-air interface, (iii) creation of the traps in the bulk of the film due to photo-structural changes. In the first two cases it is assumed that a layer of positive charge at the surface or interface in the unexposed films gives rise to surface or interface accumulation layers of higher conductivity. Upon exposure, the photoelectrons neutralize these charges thus removing the band bending; the conductivity in this case would be the true bulk conductivity. However, this band bending is not always present. Comparison of the field effect on the film substrate interface and on the top by Guha *et al* (1980) has indicated that band bending is negligible in their films. The third explanation invokes the creation of new states when the sample is exposed to light. This has been shown to take place in the case of Schottky barriers fabricated on a-Si:H, in which the series resistance increases upon exposure to light (Jousse *et al* 1980). In our case the change in σ

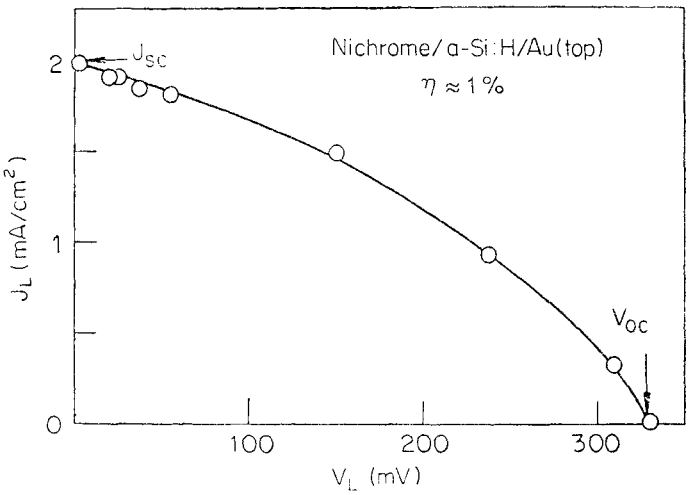

Figure 7. Load characteristic of NiCr/s-Si:H/Au (top) photovoltaic cell.

upon exposure to light is smaller in vacuum than in air. This shows that the surface states do play a role. However, at present it is difficult to say if any or all of the above mechanisms are operative in our films. Further, although the Staebler-Wronski effect in our films is much smaller than is usually seen by others using argon silane mixture (Staebler and Wronski. 1977; Tanilian *et al* 1978), it is of the same order of magnitude as reported by Guha *et al* 1981 who used a mixture of 10% SiH_4 in hydrogen. Thus it appears that the variation in composition of gas mixture alone cannot fully explain the discrepancy. Other preparation conditions, (*e.g.* the glow discharge conditions) might be responsible for different quality films obtained by different workers.

The conversion efficiency of our devices is about 1%, which appears to be smaller than the best value of 5·5% reported in the literature (Carlson 1977). The efficiency of a photovoltaic device depends upon various factors such as substrate material, barrier metal, etc. Further, the high efficiency devices prepared by others have anti-reflection coating at the top to avoid the reflection of light from the surface. We have not yet strived to improve these conditions in our case. But the stability of our films against light exposure might be taken as an indication that if these factors are improved, we might be able to improve the efficiency of our photovoltaic device considerably. An exhaustive study for optimization of all these parameters is in progress.

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Note added in proof

Using palladium as the top contact, we have recently been able to get $\eta = 4{\cdot}5\%$ for NiCr/*a*–Si:H/Pd Schottky barrier solar cells, without antireflection coating.