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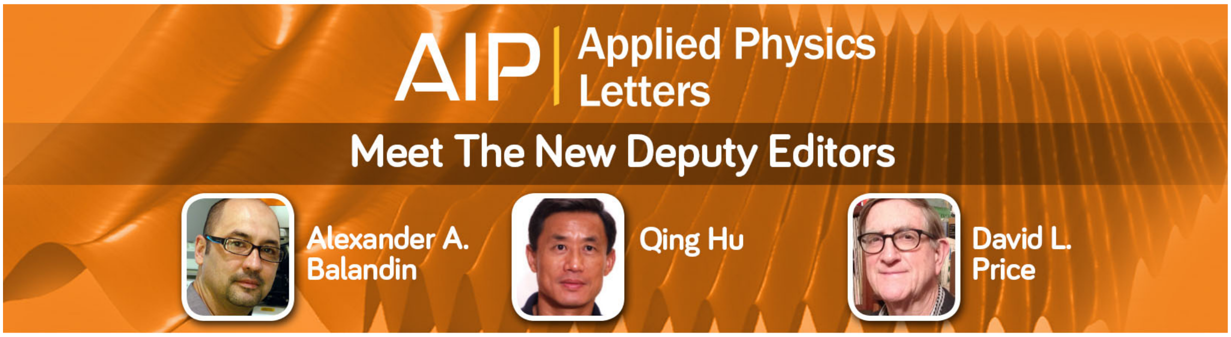

Low-cost technique for preparing n-Sb_2S_3/p-Si heterojunction solar cells

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The first fabrication of low cost n-Sb_2S_3/p-Si heterojunction solar cells by chemical deposition method is reported. It is observed that in the case of n-Sb_2S_3 films chemically deposited with silicotungstic acid on p-Si and annealed, the photovoltaic properties of the n-Sb_2S_3/p-Si junctions are considerably improved. Under AM1 illumination, the improved junction exhibited an efficiency (η) of $\sim 5.19\%$ on an active area of 0.05 cm^2 without any antireflection coating whereas the n-Sb_2S_3 films deposited without STA on p-Si showed $\eta = 1.03\%$.

Heterojunctions fabricated on various single crystalline substrates including p-Si have attracted considerable attention due to the ability of improving the junction properties of other counterparts in solar cell and optoelectronic device applications. Such heterojunctions have been fabricated by a variety of techniques such as molecular beam epitaxy (MBE),[1] metalorganic chemical vapor deposition (MOCVD),[2] photoassisted MBE,[3] electrodeposition,[4] and spray pyrolysis.[5] These heterojunctions are mainly based on III-V, II-VI, or I-III-VI compounds and are expensive. There are no reports available in the literature on the fabrication of heterojunction by chemical deposition on p-Si with n-Sb_2S_3 films. The chemical deposition method has been proved to be the least expensive, low temperature method, nonpolluting, and relatively simple for fabricating large area heterojunctions. Results reported from this laboratory[6-9] have shown that good quality n-Sb_2S_3 thin films could be achieved by chemical deposition on conducting substrates from a chemical bath containing silicotungstic acid (STA). Our recent results[9] have shown that the improvements of the n-Sb_2S_3 film quality manifest also in the properties of Schottky diodes. In the present work, we report for the first time the fabrication of n-Sb_2S_3/p-Si heterojunction solar cells and a considerable improvement on the photovoltaic properties when polycrystalline n-Sb_2S_3 films have been chemically deposited on p-Si with 10^{-5} M STA in the bath.

The p-Si substrate used for the fabrication of n-Sb_2S_3/p-Si heterojunction was (111) oriented boron doped (Photec, Mantes-La-Jolie, France) with an acceptor concentration of $N_a \approx 5.8 \times 10^{18}$ cm^{-3}. The lapping and polishing were accomplished successively by emery powder, zirconium oxide powder, a diamond paste of various grain sizes down to 0.25 μm. The mechanochemical polishing and final etching was carried out as reported earlier.[10] The n-Sb_2S_3 films with and without STA were deposited on p-Si substrate from an ammoniacal solution containing potassium antimonyl tartarate, triethanolamine, thioacetamide with or without STA as reported earlier.[6,7] The n-Sb_2S_3 films deposited with and without STA and with minimal homogeneous reaction are pinhole free, strongly adherent to the Si substrate, and are highly photoconducting particularly for the films deposited with STA. The formation of low-resistance ohmic contacts to n-Sb_2S_3 films was achieved by a copper-salt-doped graphite paste as the contact material. Subsequent to the deposition and thermal annealing (350 °C in N_2 ambient) of n-Si_2S_3 films, the devices of about 0.05 cm^2 area were isolated, and the graphite paste grid lines were printed on top of the Sb_2S_3 layer to a thickness of ~ 2 μm. The total estimated shading to the grid lines was about 12%. The device structure was thermally annealed at 120 °C in N_2 ambient for the reproducibility of the results. The configuration of the n-Sb_2S_3/p-Si heterojunction solar cell is shown in Fig. 1. The I-V measurements were carried out using a Keithley 610C Electrometer, a Keithley 163 DMM, and 225 current source. Several current measurements were taken for each voltage step to improve the signal-to-noise ratio in the very low-current regime. The capacitance measurements as a function of applied voltage (C-V) at 1 MHz were made using a Schlumberger SI 1255 HF response analyzer with Solartron 1286 electrochemical interface. The experiments were controlled by Altech microcomputer via an IEEE 488 bus.

X-ray diffraction (XRD) spectra of the as deposited (with and without STA) indicated that n-Sb_2S_3 films were amorphous in structure but the films when annealed at 350 °C in N_2 ambient showed polycrystalline with peak characteristics of orthorhombic structure. The ratio of (221) and (211) peak heights was 10:3.8 in STA deposited and subsequently annealed films but for corresponding thermally annealed films without STA was only 3:2. Since this ratio can be taken as an indication of grain orientation and crystalline quality, it may be deduced that the films

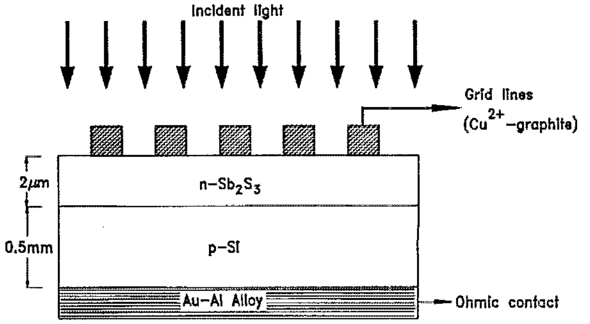

FIG. 1. Schematic view of the n-Sb_2S_3/p-Si heterojunction solar cells.

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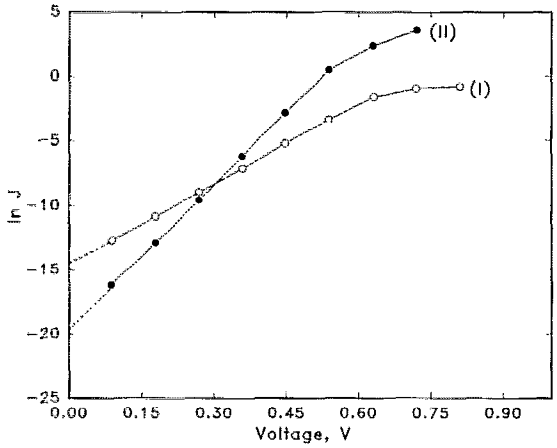

FIG. 2. Dark ln *J-V* characteristics (forward bias) at 300 K for *n*-Sb_2S_3/*p*-Si heterojunctions; (i) for the Sb_2S_3 films deposited without STA: barrier height (ϕ_b) = 0.72 eV, $J_0 = 4.5 \times 10^{-7}$ A/cm^2 and ideality factor (*n*) = 2.04 and (ii) for the Sb_2S_3 films deposited with STA: barrier height (ϕ_b) = 0.91 eV, $J_0 = 3.2 \times 10^{-9}$ A/cm^2, and ideality factor (*n*) = 1.15.

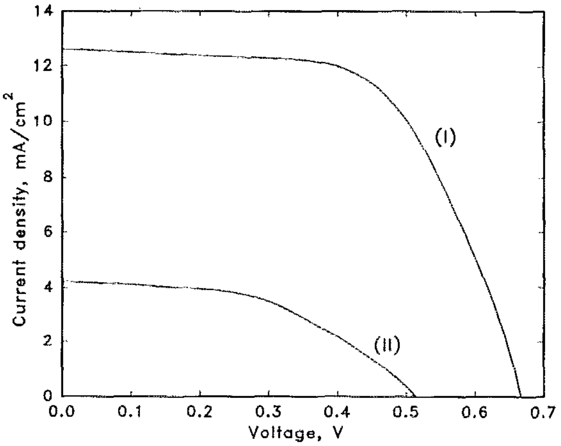

FIG. 3. Illuminated *I-V* characteristics of *n*-Sb_2S_3/*p*-Si heterojunction devices; (i) for the Sb_2S_3 films deposited with STA: $V_{oc} = 0.66$ V, $J_{sc} = 12.6$ mA/cm^2, FF = 62.4%, and efficiency (η) = 5.19% and (ii) for the Sb_2S_3 films deposited without STA: $V_{oc} = 0.51$ V, $J_{sc} = 4.2$ mA/cm^2, FF = 48.2%, and efficiency (η) = 1.03%.

deposited with STA are much more preferentially oriented along (221) than without STA used films.

The chemical compositions of the annealed films determined by x-ray photoelectron spectroscopy (XPS) and neutron activation analysis (NAA)[6,8] showed that the films formed without STA were deficient in antimony (Sb:S = 2:3.5) whereas the films with STA showed nearly stoichiometric. The presence of WO_3 (triclinic phase) has also been identified in the STA deposited films by XRD and XPS analysis and the depth profiling by XPS has indicated that WO_3 is uniformly doped along the depth of the films.[6] Resistivities of the films deposited with and without STA on glass substrate were determined by four-point probe van der Pauw method and found to be 5.0 $\times 10^6$ and 5.3×10^6 Ω cm, respectively. Optical absorption studies were carried out by a Shimadzu (UV/Vis) spectrometer for both the films deposited with and without STA and subsequently annealed at 350 °C in N_2 atmosphere. A sharp absorption edge at 1.72 eV was obtained for the STA deposited films but no sharp absorption was found for the films deposited without STA. With tungsten-halogen lamp (AM1) illumination, the photoconductivity ratio of Sb_2S_3 films deposited with STA is in the range of 10^3–10^4, whereas the *n*-Sb_2S_3 films deposited without STA is approximately two orders of magnitude lower.

Typical *I-V* characteristics of the junctions formed on *p*-Si with *n*-Sb_2S_3 (without and with STA) are shown in Fig. 2 [(i) and (ii)]. Both curves show rectifying behavior in the dark. From the forward ln $J - V$ characteristics [Fig. (i)], the ideality factor (*n*) was found to be 2.04 and the saturation current density (J_0) = 4.5×10^{-7} A/cm^2. (ii) represents the corresponding *I-V* characteristics of the heterojunction using *n*-Sb_2S_3 films with STA. Good rectification was also obtained for the *n*-Sb_2S_3 films with STA. The values of *n* and J_0 were 1.15 and 3.2×10^{-9} A/cm^2, respectively. The ideality factors for both with and without STA heterojunctions were found to be $n > 1$ at $V < 0.6$ V. This indicates that processes other than thermionic emission, such as image-induced barrier lowering or tunneling may partly be responsible for charge transport across the heterojunction. Another possibility to the nonideality stems from carrier recombination in the depletion region of the junction.

Figure 3 [(i) and (ii)] shows the *I-V* characteristics of the two cells with the Sb_2S_3 films with and without STA, under AM1 tungsten-halogen illumination. The best solar cell parameters obtained under AM1 illumination from a series of *n*-Sb_2S_3/*p*-Si devices (with and without STA) were (i) for the films with STA, $J_{sc} = 12.6$ mA/cm^2, $V_{oc} = 0.66$ V, FF = 0.624 giving the efficiency (η) = 5.19% and (ii) for the films without STA, $J_{sc} = 4.2$ mA/cm^2, $V_{oc} = 0.51$ V, FF = 0.482 showing the efficiency (η) = 1.03%. The device parameters reported here were measured by following identical conditions of device fabrication steps except the *n*-Sb_2S_3 films prepared with and without STA. So, the significant influence of STA during the film preparation is distinctly visible. The optimization of the device parameters with the junction preparation conditions and the deposition of antireflection coating on top of the device structure is under study.

The evidence of the barrier modification is seen in the 1 MHz *C-V* characteristics of the devices. The $1/C^2$-*V* plots for the devices are shown in Fig. 4 [(i) and (ii)]. The heterojunction formed with *n*-Sb_2S_3 films with STA [(i)] showed higher intercept voltage V_i of 0.62 V, giving a barrier height (ϕ_b) of 0.92 V, whereas for the *n*-Sb_2S_3 films without STA showed V_i of 0.44 V and $\phi_b = 0.74$ V. From the slope of the curves, the carrier concentrations were estimated to be 2.3×10^{12} and 1.05×10^{12} cm^{-3}, respectively. These values are consistent with the values determined by Hall measurements.

The lattice mismatch of *n*-Sb_2S_3/*p*-Si heterojunctions obviously results in nonepitaxial growth for the film thicknesses reported here. Further, a large density of electrically active interface states is expected. Both interface defects and bulk traps reduce the voltage intercept in the $1/C^2$ vs

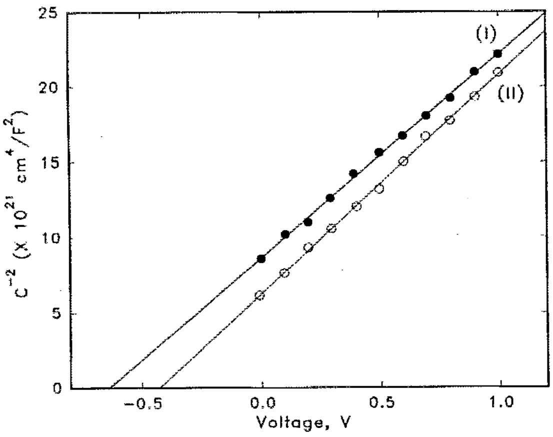

FIG. 4. $1/C^2$ vs V characteristics (reverse bias) at 300 K for n-Sb_2S_3/p-Si heterojunctions; (i) for n-Sb_2S_3 films deposited with STA and (ii) for n-Sb_2S_3 films deposited without STA.

V curves. The formation of the WO_3 interfacial layer as confirmed by XPS and NAA[7,8] studies possibly plays an important role in the electronic charge transfer processes of the device leading to an improved photovoltaic performance including the enhanced ϕ_b and η.

In conclusion, we have demonstrated the low cost fabrication of the n-Sb_2S_3/p-Si heterojunction device by a chemical deposition of n-Sb_2S_3 thin films on p-Si substrates. From the preliminary results, it may be concluded that the heterojunction structure described in this letter have high promise for the manufacturing of low cost solar cells. Further studies on the mechanisms of the carrier transport across the junction are under current investigation.

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