IMPROVED SCHOTTKY BARRIER ON n-Sb_2S_3 FILMS CHEMICALLY DEPOSITED WITH SILICOTUNGSTIC ACID

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Indexing terms: Solar cells, Diodes, Semiconductor devices

The first fabrication of low cost Schottky barrier solar cells on chemically deposited polycrystalline n-Sb_2S_3 thin films is reported. It is observed that in the films deposited with silicotungstic acid and annealed, the Schottky barrier height (ϕ_b) of the Au/n-Sb_2S_3 junctions is considerably improved from 0·54 to 0·76 eV. The ideality factor n decreased from 2·32 to 1·08 and the reverse-saturation current density J_0 from $3{\cdot}2 \times 10^{-6}$ to $1{\cdot}5 \times 10^{-9}\,A\,cm^{-2}$. Under AM1 illumination, the improved diode exhibited a conversion efficiency of ~3%.

Considerable effort has been made recently in understanding the properties of Schottky barriers and in the enhancement of barrier height ϕ_b, especially with the view to increasing the open-circuit voltage V_{oc} of solar cells. The most widely used technique has been the growth of intervening thin oxide layers [1–2]. This however results in an increase of the ideality factor n and the reverse-saturation current density J_0. In this Letter, we demonstrate for the first time a considerable overall improvement in the properties of the Au/n-Sb_2S_3 Schottky barrier solar cells when highly photoconducting and polycrystalline n-Sb_2S_3 films have been deposited with 10^{-5} M silicotungstic acid (STA) in a chemical bath. The subsequent heat treated n-Sb_2S_3 films shown a significant decrease of both n and J_0 with an increase in ϕ_b as found through I–V and C–V measurements.

The films were characterised through resistivity and Hall-effect measurements as reported earlier [3–4]. All thin film ITO/n-Sb_2S_3/Au Schottky junctions were fabricated in the following manner. ITO coated glass slides were cleaned with isopropyl alcohol, acetone and deionised water; 2·2 μm thick n-Sb_2S_3 films (with and without STA) were then deposited from four successive fresh deposition baths. The resulting films were thermally annealed at 300°C for 1 h in N_2 ambient. Gold films (6N) of 250 ± 10 Å thickness were deposited by vacuum evaporation onto n-Sb_2S_3 films at 100°C. The Schottky junctions were prepared using a proper masking arrangement so as to form a circular device having an active area of 0·04 cm^2. The I–V measurements were carried out using a Keithley 610C Electrometer, a Keithley 163 DMM and 225 current source. The capacitance measurements as a function of applied voltage (C–V) at 1 MHz were made using a Schlumberger SI 1255HF frequency response analyser with Solartron 1286 electrochemical interface. The experiments were controlled by an Altech microcomputer via an IEEE 488 bus.

The J–V characteristics of the Schottky diode are given by

$$J = J_0[\exp(qV/nkT) - 1] \qquad (1)$$

where J_0 is the reverse-saturation current density and can be expressed as

$$J_0 = A^{**}T^2 \exp(-q\phi_b/nkT) \qquad (2)$$

where A^{**} is the effective Richardson constant and ϕ_b the Schottky barrier height.

The J–V characteristics were measured between 300 and 450 K from which ln J against V curves were obtained. The barrier heights ϕ_b and A^{**} were determined from ln (J_0/T^2) against $1/T$ plots (Fig. 1) and included in Table 1.

The values of ϕ_b determined from the forward and reverse I–V characteristics at 300 K were in good agreement, being 0·52 and 0·54 eV, respectively, for the annealed n-Sb_2S_3 films without STA (Table 1). The $1/C^2$ against V plot was found to be linear and gave $\phi_b = 0{\cdot}57$ eV, with $N_d = 1{\cdot}2 \times 10^{12}\,cm^{-3}$. The difference between the ϕ_b values measured by different methods is within the usual range reported, the lower values of ϕ_b in the reverse bias measurements being due to barrier lowering and edge leakage.

STA incorporated Sb_2S_3 Schottky diodes showed similar plots giving $\phi_b = 0{\cdot}76$ eV from reverse bias characteristics at 300 K. The Mott-Schottky plot gave a value of 0·74 eV. The ideality factor n at 300 K was found to be reduced from 2·32 to 1·08 while J_0 decreased from $3{\cdot}2 \times 10^{-6}$ to $1{\cdot}5 \times 10^{-9}\,A\,cm^{-2}$. The J–V characteristics were found to be unchanged after temperature cycling up to 540 K indicating that the effects due to the STA were stable.

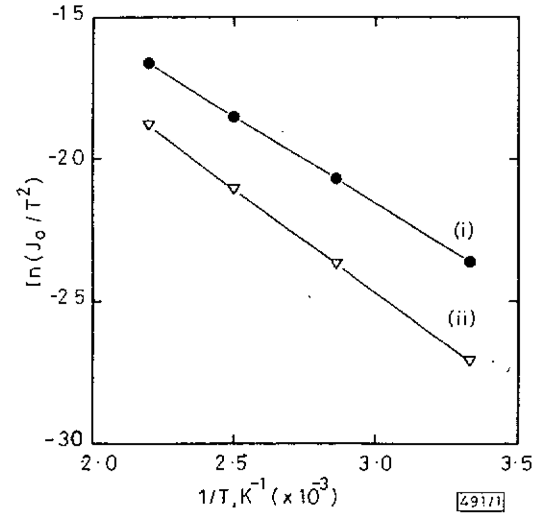

Fig. 1 *ln (J_0/T^2) against 1/T for Au/n-Sb_2S_3 Schottky barriers*

(i) n-Sb_2S_3 films with STA
(ii) n-Sb_2S_3 films without STA

Table 1 SCHOTTKY BARRIER HEIGHT ϕ_b AND IDEALITY FACTOR n BOTH WITH AND WITHOUT STA INCORPORATED Au/n-Sb_2S_3 DIODES

	Ideality factor n		Barrier heights ϕ_b	
Temperature	Without STA	With STA	Without STA	With STA
K			eV	eV
300	2·32	1·08	0·54	0·76
350	2·21	1·09	0·56	0·78
400	2·18	1·07	0·55	0·78
450	2·16	1·08	0·56	0·76

Fig. 2 shows the illuminated (AM1) I–V characteristics for the Au/n-Sb_2S_3 Schottky junctions. The diode fabricated with the films deposited from the STA bath showed the best photovoltaic performance with short-circuit photocurrent density J_{sc} of 7·85 mA/cm^2, and open-circuit voltage V_{oc} of 0·68 V with a fill factor of 0·56. The resulting conversion efficiency η at

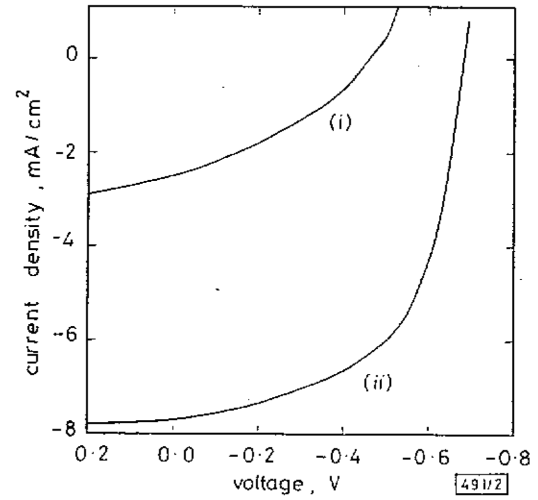

Fig. 2 *Current-voltage characteristics of Au/n-Sb_2S_3 diode at AM1*

(i) annealed (300°C in N_2 atmosphere for 1 h) Sb_2S_3 films without STA
(ii) annealed (300°C in N_2 atmosphere for 1 h) Sb_2S_3 films with STA

300 K was 3% whereas the diode fabricated with the films without STA showed $\eta \simeq 0{\cdot}4\%$.

The experimental results show significant improvement of the Schottky diode and photovoltaic parameters on Sb_2S_3 films deposited with STA: a reduction of n from 2·32 to 1·08, a decrease of J_0 from $3{\cdot}2 \times 10^{-6}$ to $1{\cdot}5 \times 10^{-9}\,A\,cm^{-2}$. This may be attributed to a significant decrease of surface recombinations. The chemical compositions of the samples are probably responsible for this effect. Effectively, the XRD, NAA and XPS measurements [3–4] have shown the presence of WO_3 (triclinic phase) in the films deposited with STA and the depth profiling by XPS has indicated that WO_3 is uniformly doped along the depth of the films. Such interfaces are probably not very different from other oxide-terminated surfaces (e.g. Si/SiO_2 interface), which exhibit low surface recombination velocity. The wide-bandgap oxide serves to open the energy gap at the interface thus pushing the surface states out of the bandgap of n-Sb_2S_3. Similar results for the effect of oxide layers on the Schottky diode characteristics were obtained for Si and InP Schottky devices, investigated by Pande [5] and Wada *et al.* [2]. The results were interpreted on the basis of the incorporation of negative charge into the oxides and are in close agreement with out previous observations [3–5]. We have shown that incorporating STA during the chemical deposition of semiconductor films significantly improved their electrochemical barrier properties, which are in many ways similar to those of Schottky barriers [3–5].

In conclusion, the presented experiments demonstrate the beneficial effects of STA in growing good quality n-Sb_2S_3 films and a low cost method of fabricating improved n-Sb_2S_3/Au Schottky diodes. The results could also be of technological significance in Sb_2S_3 MIS devices and be applied to other semiconductors and their devices.

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NEW NUMBER THEORETIC TRANSFORM

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A new number theoretic transform is introduced. This transform is defined modulo the Mersenne primes, has long transform length which is a power of two, a fast algorithm, and the inverse transform has within a factor of $(1/N)$ the same form as the forward transform. Thus, it is well suited for the calculation of error free convolutions and correlations.

Introduction: One of the most important properties of fast transforms with the cyclic convolution property (CCP) is their ability to reduce considerably the number of multiplications and additions in the computation of convolutions and correlations, resulting in faster calculations.

In this Letter a new transform is introduced having the CCP, defined modulo the Mersenne primes and having a fast algorithm. This allows the fast calculation of error free long convolutions.

Definition of new transform: The transform is defined as

$$X(k) = \sum_{n=0}^{N-1} x(n)(\beta_1(nk) + \beta_2(nk)) \quad \mathrm{mod}\ M_p \tag{1}$$

Here M_p is a Mersenne prime:

$$\beta_1(nk) = \mathrm{Re}\ [(\alpha_1 + j\alpha_2)^{nk}]$$

and

$$\beta_2(nk) = \mathrm{Im}\ [(\alpha_1 + j\alpha_2)^{nk}] \tag{2}$$

Also, $\alpha_1 = 2^q$, $\alpha_2 = (-3)^q$, $q = 2^{p-2}$ mod M_p.

Eqn. 2 corresponds to α_1 and α_2 of order $N = 2^{p+1}$ as given for complex transforms in Reference 4. For length N/d, $\beta_1(nk)$ and $\beta_2(nk)$ are given by

$$\beta_1(nk) = \mathrm{Re}\ [((\alpha_1 + j\alpha_2)^d)^{nk}]$$

and

$$\beta_2(nk) = \mathrm{Im}\ [((\alpha_1 + j\alpha_2)^d)^{nk}]$$

where Re [ ] and Im [ ] stand for real and imaginary parts. The modulus M_p is one of the well known Mersenne primes.

The transform length is an integer power of two and can be of length up to $N = 2^p$. This contrasts with other real transforms based on the Mersenne primes which have rather short transform lengths [1, 2]. The emphasis on Mersenne numbers in this Letter is due to the fact that arithmetic operations and residue reduction modulo Mersenne numbers are simpler and easier to implement than other moduli.

The inverse transform is of the same form as the forward transform except for a multiplying term $(1/N)$.

$$x(n) = (1/N) \sum_{k=0}^{N-1} X(k)(\beta_1(nk) + \beta_2(nk)) \quad \mathrm{mod}\ M_p \qquad n = 0, 1, 2, \ldots, N-1 \tag{3}$$

Convolution property: The new transform has the cyclic convolution property and can be used to calculate the convolution of a data set $x(n)$ and filter impulse response $h(n)$:

$$\begin{aligned} y(n) &= x(n) * h(n) \\ &= \textit{inverse-new-transform}\ \{X(k) \otimes H_{2ev}(k) \\ &\qquad + X(N-k) \otimes H_{2od}\} \end{aligned}$$

This can be shortened to

$$y(n) = \textit{inverse-new-transform}\ \{X(k)\Gamma H(k)\} \tag{4}$$

where

$$H_{2ev}(k) = \{H_2(k) + H_2(N-k)\}/2 \quad \mathrm{mod}\ M_p \tag{5}$$

$$H_{2od}(k) = \{H_2(k) - H_2(N-k)\}/2 \quad \mathrm{mod}\ M_p \tag{6}$$

If the impulse response of the filter used is symmetric, eqn. 4 becomes

$$y(n) = \textit{inverse-new-transform}\ \{X(k) \otimes H(k)\} \tag{7}$$

where $\otimes$ is point by point multiplication.

As in all number theoretic transforms, $x(n)$ and $h(n)$ should be scaled so that the convolution result $|y(n)|$ never exceeds $M_p/2$; one suggested upper bound is given in Reference 3.