AMORPHOUS SILICON FILMS ON COPPER, NICKEL AND STAINLESS STEEL SUBSTRATES BY ELECTRODEPOSITION

Prakhya R. Sasi, T.R. Rama Mohan and S. Venkatchalam

Department of Metallurgical Engineering, Indian Institute of Technology, Bombay 400 076, India

Thin and uniform films of amorphous silicon are obtained on Cu, Ni and stainless steel substrates by electrodeposition using fluosilicic acid in ethylene glycol bath. The deposition process is studied by varying the current density and electrolyte concentration. The films are characterized for structure and composition. The analysis by ESCA showed the presence of fluorine in the films.

Silicon is a good semiconductor material used in many applications. Of late, amorphous silicon (a-Si) is getting increased attention for application in electronics and photovoltaic industry [1,2]. Amorphous silicon can be deposited as thin films by various techniques such as r.f. glow discharge, decomposition of silane, chemical vapour deposition (C.V.D.), sputtering, etc. [3-6]. However the silicon obtained by these processes is expensive.

Electrodeposition of amorphous silicon, on the other hand seems to be a feasible approach for the development of low cost and large area thin films. Electrodeposition process has a number of advantages when compared to other techniques and is inexpensive.

Kroger et al [7] reported the electrodeposition of a-Si from non-aqueous electrolytes containing $SiCl_4$, tetra ethyl orthosilicate and ammonium hexaflourosilicate. Cohen and Huggins [8] reported the epitaxial growth of silicon from molten fluorides by electrodeposition. Austin and Agarwal [9] electrodeposited the amorphous silicon using silicon halides in aprotic solvents. Rama Mohan and Kröger [10] reported the cathodic deposition of a-Si from an electrolyte containing tetraethyl orthosilicate and ethylene glycol and/or formamide.

The present paper deals with studies on the electrodeposition of a-Si using an electrolyte consisting of H_2SiF_6 dissolved in ethylene glycol. Deposits are obtained under varying current densities and electrolyte concentrations for different combinations of cathodes and anodes.

EXPERIMENTAL

The deposition is carried out using an analytical reagent grade ethylene glycol and fluosilicic acid (H_2SiF_6) (31 percent solution). Platinum and graphite are used as anodes and thin strips of 0.2 mm thick pieces of Ni, Cu and stainless steel of area 1 cm^2 are used as cathodes. The cathode is polished on 1/0, 2/0, 3/0 and 4/0 emery papers to a mirror finish, washed thoroughly with water and acetone before weighing, and using for electrodeposition. After the deposition is completed, the cathode is again washed in acetone, dried, cooled before weighing again. The interelectrode distance is kept at 2 cms and the time of deposition each case is 1 hour. The electrolytic cell is kept in a water thermostat ($32 \pm 2°C$).

Preliminary experiments are carried out to determine the optimum concentration of H_2SiF_6 required in the electrolyte for getting an appreciable amount of deposition. The concentration of H_2SiF_6 in these preliminary experiments is varied from 0.03 M to 0.1 M in ethylene glycol in steps of 0.03 M. It is found that appreciable amount of deposition occured only from 0.1 M. So further experiments were carried out in the range 0.1-0.5 M. To study the effect of varying current density on deposition, the current density is varied from 50 mA/cm^2 to 250 mA/cm^2 in regular steps.

RESULTS AND DISCUSSION

The influence of current density and concentration of the electrolyte on the weight of the material deposited is shown in Figure 1 for graphite-stainless steel, in Figure 2 for graphite-copper and in Figure 3 for platinum-nickel electrode systems.

0013 466 x 33 (36) 233-236

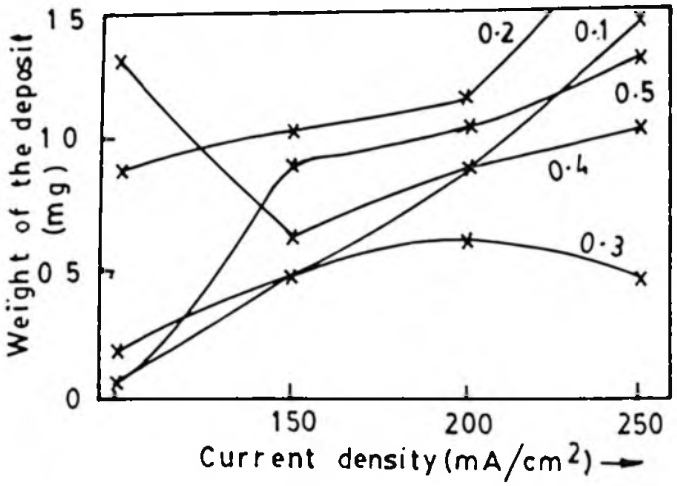


Fig. 1 Effect of current density on weight of the deposit for graphite-stainless steel Electrode System

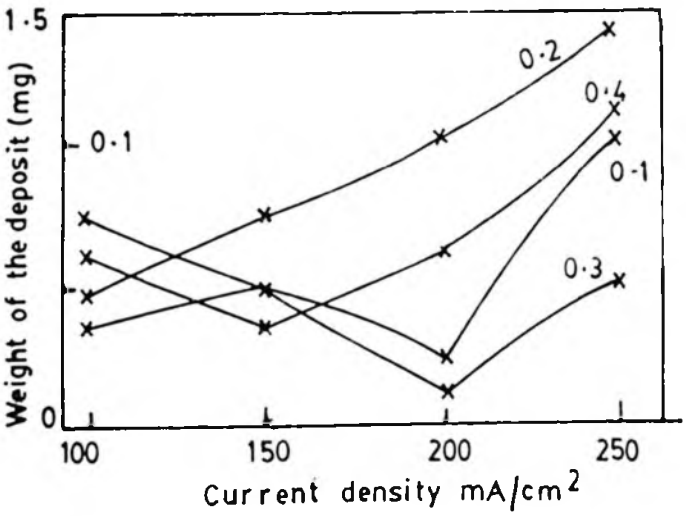


Fig. 2 Effect of current density of weight of Deposit for graphite copper electrode system

It is seen from the above figure that in most cases the deposition weight is increased with increased current density.

It is observed that as the concentration of H_2SiF_6 increases, the bath becomes more conducting as seen by the observed decrease in cell voltage with increase in H_2SiF_6 at a given current. Further as seen from these figures, the weight of the deposit decreases at higher concentrations of H_2SiF_6 in ethylene glycol. It is worth noting that the weight of

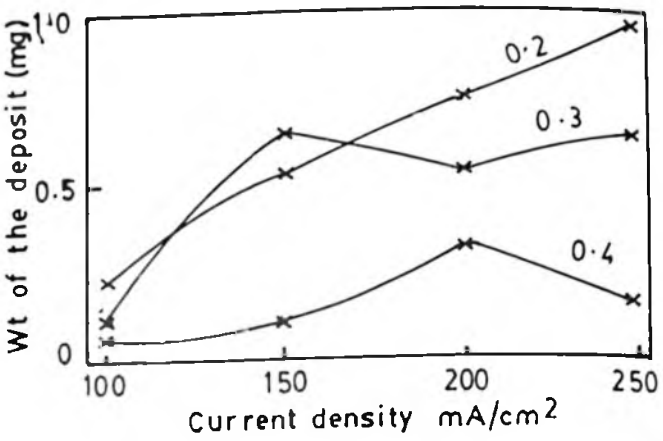


Fig. 3 Effect of current density on weight of the deposit for platinum - nickel electrode system

the deposit is more at 0.2 M concentration in all cases of the present series of experiments and this is in confirmation with the published results [8,9]. It is likely that at higher concentrations, there are some association reactions which result in decrease of deposits.

To understand the decrease in yield of deposit at higher H_2SiF_6 concentration, the various reactions occuring in the cell have to be considered.

In the solution the following equilibria exist.

$$H_2SiF_6 \rightleftharpoons 2\,H^+ + (SiF_6)^{2-} \qquad ...(1)$$

$(SiF_6)^{2-}$ would associate with strong hydroxyl group of glycol and eventually a series of cationic $(SiF_4)^{4-x}$ species result thus.

$$(SiF_6)^{2-} \rightleftharpoons (SiF_3)^+ + 3F^- \qquad ...(2)$$

$$(SiF_3)^+ \rightleftharpoons (SiF_2)^{2+} + F^- \qquad ...(3)$$

$$(SiF_2)^{2+} \rightleftharpoons (SiF)^{3+} + F^- \qquad ...(4)$$

$$(SiF)^{3+} \rightleftharpoons Si^{4+} + F^- \qquad ...(5)$$

The water present in the solution also ionizes according to the equation (6)

$$H_2O \rightleftharpoons H^+ + OH^- \qquad ...(6)$$

In addition there is one more reaction possible from the products

$$H^+ + F^- \longrightarrow HF \qquad ...(7)$$

The cathodic reactions are

$$2H^+ + 2e \rightleftharpoons H_2 \quad \ldots(8)$$

$$SiF_3^+ + e \longrightarrow a\text{-}SiF_3 \quad \ldots(9)$$

$$SiF_2^{++} + 2e \longrightarrow a\text{-}SiF_2 \quad \ldots(10)$$

$$SiF^{3+} + 3e \longrightarrow a\text{-}SiF \quad \ldots(11)$$

$$Si^{4+} + 4e \longrightarrow a\text{-}Si \quad \ldots(12)$$

The anodic reactions are

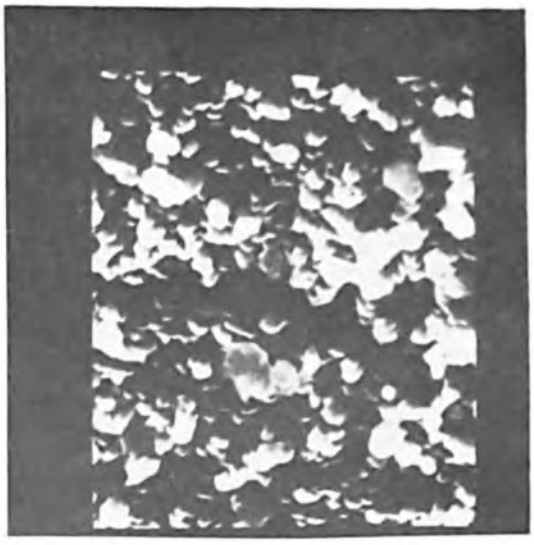
$$2OH^- \longrightarrow H_2O + 1/2\,O_2 + 2e \quad \ldots(13)$$

$$6F^- \longrightarrow 3F_2 + 6e \quad \ldots(14)$$

At higher concentrations of H_2SiF_6, there is a greater concentration of F^- and reaction (7) becomes predominant. The formation of HF in the bath is likely to redissolve deposited silicon. The increased conductivity of the bath coupled with anodic gas evolution is likely to render the bath acidic and hence causing the silicon to redesolve in the bath at higher concentrations of the electrolyte.

It is observed that the films are uniformly coated and colour of the deposits is changed from greyish yellow to black as the concentration increases. The films are characterized for structure and composition. The XRD analysis showed the amorphous nature of the films. The SEM (Scanning Electron Microscope) photograph of the deposit at 4000 K is shown in Figure 4. The thickness of the deposits are calculated assuming the density of a-Si to be 2.32 gm/cm^3 . The calculated values vary from 0.4 um (for 0.1 mg deposit) to 5.2 μm (for 1.2 mg deposit). But the actual thickness of the films seem to be somewhat different from the calculated values. This may be due to the effects of HF and gas evolutions.

The deposits are characterized by using ESCA (Electron Spectroscopy for Chemical Analysis) and EDAX (Energy Dispersive Analysis of X-rays) techniques. The ESCA is used to ascertain the elemental composition on the surface while EDAX quantifies the elemental composition of the films. The EDAX analysis showed the presence of calcium impurity in the films in the range of 4 to 9% particularly when graphite is used as anode. The calcium content is negligibly small when platinum is used as the anode.



The deposit at 4,000X.

Fig. 4 Scanning electron microscope photograph of amorphous silicon film for graphites-stainless steel electrode system at 0.2 M and 150 mA/cm^2

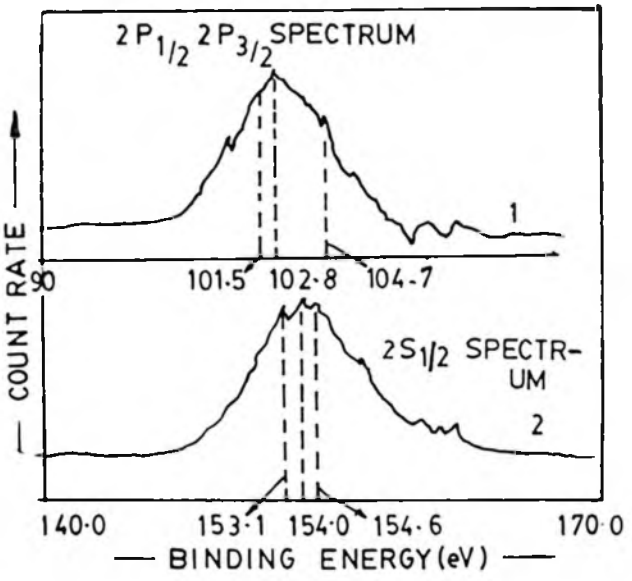


Fig. 5 ESCA Spectra of the electrodeposited Amorphous silicon film

Source Al K, Voltage 12.5kV, i = 20mA, E = 50ev, Slits 4 mm, Time 300 sec, Counts 3 x 10^3/sec.

While using ESCA, the quantitative characterization of the deposits is done by comparing the positions and shifts of the peaks of different elements with those of standard values. Figure (5) shows the silicon 2s and 2p spectra of amorphous silicon. The

silicon 2p spectrum shows the peaks in the range of 101.5 eV to 105 eV which are shifted from the standard values (99 eV and 100 eV) for 2 $P_{1/2}$ and 2 $P_{3/2}$ levels respectively. These shifts from the actual values indicate that silicon is present in the deposits as a compound. The 101.5 eV 103 eV values correspond to the peaks formed by silicon fluoride compounds (SiF_x). The silicon $2S_{1/2}$ spectrum also shows similar trends confirming the above mentioned nature of the samples. The presence of fluoride in the samples may serve as a dangling bond terminator and hence improving the quality of the films.

REFERENCES

1. Y. Hamakawa, *Proc. of 17th IEEE Photovoltaic Specialists Conference*, Kissimmee, Florida U.S.A., (1984) p-63.
2. M. Ohnishi, H. Nishiwaki, S. Tsuda, N. Nakamura, S. Nakane, T. Matsuka and Y. Knwano, *Reference (1)* pp 70.
3. D.L. Williamson and S.K. Deb, *J. Appl.Phys* **54** (1983) 2588.
4. V.L. Dalal, M. Akhpar and A. Dalahoy, *Proc. 16th IEEE Photovoltaic specialists Conference, San Diego,* (1982) 1385.
5. Y. Chashi, J. Kenne, M. Konagai and K. Takahashi, *Appl. Phys. Lett.* **42** (1983) 1028.
6. E. Sabisky, W. Wallace, A. Mihaail, H. Mohan and S. Tsuo, *Reference (1)* p-217.
7. F.A. Kroger Annual Report Prepared for ERDA under contract EX-76-8-03-011 3 PA 40, Aug. 1979, *Dept. of Materials Science, University of Southern California Univ. Park, Lose Angles CA 90007*, U.S.A.
8. U. Cohen and R.A. Huggins, *J. Electrochem. Soc.*, 123 (1976) 381.
9. A.E. Austin and A.K. Agarwal, *J. Electrochem. Soc.*, 128 (1981) 2292.
10. T.R. Rama Mohan and F.A. Kröger, *Electrochem. Acta*, 27 (3) (1982) 371.

AWARD FUND

ELECTROCHEMICAL SOCIETY OF INDIA AWARD FUND

has been created by the Society
for presenting awards annually
to the authors of the best papers in different disciplines
appearing in each Volume of

THE JOURNAL OF ELECTROCHEMICAL SOCIETY OF INDIA

Contributions to the above fund are solicited
from members and well wishers to augment the resources.
Donations above Rs. 250 are entitled
for exemption from income tax under clause 80 G.

Donation may be sent to the
Electrochemical Society of India