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AUGER ANALYSIS OF SILICON THIN FILMS DEPOSITED ON
CARBON AT HIGH TEMPERATURES

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ABSTRACT

Silicon films (2000-3000Å thick) were vacuum deposited onto pyrolytic graphite, extruded graphite and glassy carbon at 1150°-1200°C to test the possibility of using carbon as a substrate in thin film silicon solar cells. The distribution of silicon and carbon in the carbon-silicon interface was studied using Auger spectroscopic depth profiling. The results showed that, for all substrates, carbon diffused deeply into silicon films, and for all substrates except glassy carbon, silicon also diffused deeply into carbon. In both cases, silicon carbide is formed. Several methods to build diffusion barriers were tested. A diffusion mechanism is proposed according to which silicon atoms first form a carbide layer with the surface carbon atoms, whereafter cracking of the carbon lattice and diffusion of silicon through the carbide layers into the carbon substrates follow. This mechanism is shown to explain very well the dependence of the measured silicon and carbon contents on the structure of the carbon substrates used for depositions.

INTRODUCTION

To make thin film solar cells for terrestrial photovoltaic applications the choice of a suitable substrate material is important. Both the cost and material properties need to be considered. The substrate must be electrically conductive and also be a high temperature material if deposition techniques such as chemical vapor deposition are to be used. One possible substrate material for silicon film deposition is graphite. Graphite has been widely used as crucible material in manufacturing silicon crystals since carbon solubility in silicon is very low, being of the order of 10^{-4} at.% at 1200°C .¹ However, literature data concerning the Si-C system deal mostly with the Si bulk-C bulk properties and the situation could be quite different for systems containing thin films. This work, therefore, describes an attempt to study the Si thin film-C bulk system and the resulting diffusion of carbon into the silicon film when the latter is vacuum deposited onto the carbon substrates at the temperature region of 1150° - 1200°C . Several forms of carbon are tested for this purpose, including pyrolytic graphite, extruded graphite and glassy carbon. For the pyrolytic graphite two orientations are used for silicon deposition, the parallel-to-layers plane and the normal-to layers plane. These are referred to as the basal and edge plane, respectively.

EXPERIMENT AND RESULTS

Silicon was vacuum deposited onto carbon substrates using conventional electron beam heating. Experimental parameters such as the deposition rate monitoring, film thickness measurement, and substrate mounting and heating, etc, have been described elsewhere.² Some modification was made in this study to attain higher substrate temperatures. A hole was cut through part of the tantalum substrate holder to allow direct electron bombardment of the substrates mounted in this region. The substrate temperature could thus easily reach ca 1300°C while the bulk holder remained at ca 800°C. In addition, this allowed much faster heating of the substrates and better control of the heating time in some of the diffusion studies of this work.

In this study, the carbon substrate temperatures during deposition were kept at the region of 1150°-1200°C. Substrate temperatures were measured with an optical pyrometer and corrected for the emissivity of the substrate material, window absorption, temperature gradient on the substrate surface and fluctuations in temperature during depositions. Deposition time was 1 hr for all high temperature experiments. Silicon deposition rate was ca 50Å/min. The carbon substrates used were basal plane and edge plane pyrolytic graphite, extruded graphite and glassy carbon. All substrates were cleaned with detergent and were ultrasonified before use. Prior to deposition, the substrates were outgassed at 1250°-1300°C for 1 hr in a vacuum of 1×10^{-6} Torr. At least two runs were made for each of the high temperature depositions.

Depth profiles of silicon and carbon in both the silicon film and the carbon substrate were obtained using Auger electron spectroscopy. An Auger spectrometer from Physical Electronics was used which is equipped

with a double-focusing cylindrical mirror analyzer and an ion sputtering gun. A six-channel multiplex unit and a point plotter recorder were used to record the Auger depth profiles. Ion sputtering using argon was performed at an argon pressure of 5×10^{-5} Torr with a sputtering rate of ca 30-40 Å/min for the silicon film.

A. Silicon Deposited at High Temperature

In general, it was found that for all the carbon substrates used, the carbon content in the silicon films was much higher than expected from the solubility data of the bulk system described above. Carbon content as high as 30-50 at.% was observed in most of the silicon films deposited. The lowest carbon concentration was observed in silicon films deposited onto glassy carbon. In addition, except for glassy carbon, silicon was also found to penetrate deeply into the carbon substrates. Figure 1 shows the Auger profiles for the four types of carbon substrates studied.

The Auger peak shapes of carbon revealed that carbon due to surface contamination was graphitic.³ As the surface layers were sputtered off the observed carbon changed to the carbide form, indicating formation of silicon carbide in the silicon films.³ The carbon changed to graphitic again at a later stage of sputtering where enough material had been removed to allow an analysis of the bulk substrate. This was observed for the edge plane pyrolytic graphite, extruded graphite and glassy carbon. The basal plane pyrolytic graphite, however, showed a carbide shape Auger peak deep into the substrate. Figure 2 shows one set of carbon peaks illustrating the different peak shapes observed while sputtering through a thin silicon film on the edge plane of pyrolytic graphite. These

peaks correspond to those observed on the surface, in the silicon film and in the carbon substrate. The observed formation of silicon carbide in the silicon film is in agreement with the resistivity measurement of Chu⁴ who found an increased resistivity region in the deposited silicon film as the graphite surface was being approached. In our case, the silicon films deposited were thin, being ca 2000-3000Å thick and the results showed silicon carbide formation throughout the whole film analyzed.

As indicated earlier, the silicon deposition rate was ca 50Å/min for all samples. A silicon film with a thickness of ca 2000-3000Å was therefore expected after 1 hr of deposition if the silicon diffusion into the substrate was not significant. Significant diffusion of silicon was, however, noted for the silicon films deposited onto the pyrolytic and extruded graphites. A measurement of the actual silicon film thickness was, therefore, difficult for these substrates. In the case of glassy carbon, silicon diffusion was much less than those using graphites, and the deposited silicon film should show the expected thickness. However, the actual silicon film thickness was only about 1/4 of that expected. Work is currently in progress to understand this much lower deposition rate on glassy carbons and will be published elsewhere.

B. Building Diffusion Barriers

The formation of silicon carbide in the deposited silicon film is very undesirable in thin film solar cells because of the large band gap in silicon carbide. Efforts have, therefore, been made to build diffusion barriers on the surface of carbon substrates prior to

depositing silicon films. Two methods have been tested and a third one is in progress. These are described below.

1. Room Temperature Deposited Silicon as Diffusion Barrier

As mentioned earlier, literature data on the Si bulk-C bulk system indicated very low solubility of carbon in silicon. An attempt was, therefore, made to approach the bulk system in lowering the carbon diffusion problem. In the above silicon deposition process at high temperature, silicon atoms arriving on the carbon surface are always free to react with the latter to form silicon carbides, whereas the reaction rate could be lower if silicon was first deposited on carbon at room temperature and then heated to high temperature. The reaction rate in the latter case could approach that expected from the bulk data. Therefore, a silicon film of ca 1000Å thickness was deposited on the carbon substrate held at room temperature. The system was heated to 1150°-1200°C and another layer of Si was deposited to a total thickness of ca 3000Å. Auger analysis, however, still showed a high carbon content, comparable to those observed earlier. This is shown in Fig. 3. This indicated that the bulk properties were not reached for a silicon film of 1000Å thickness.

2. Ultrathin SiO₂ Layer as Diffusion Barrier

Next we tried to convert an extremely thin silicon layer to the oxide form and study its potential for a diffusion barrier. The advantage of this technique is the easy oxidation of the surface layers of silicon. The major drawback is the insulator property of SiO₂. Therefore, the oxidized layer has to be kept extremely thin to minimize the latter effect. A thickness of ca 10Å was chosen as a compromise between the barrier efficiency and the conduction requirement.

A silicon film of ca $20\text{\AA}$ thickness was deposited on the carbon substrate held at room temperature and exposed to air for 2 hrs to convert ca $10\text{\AA}$ to oxidized silicon.⁵ The substrate was then heated to $1150^{\circ}\text{--}1200^{\circ}\text{C}$ in vacuum, outgassed for 1 hr, and more silicon was deposited on it to a total thickness of ca $2000\text{--}3000\text{\AA}$. Auger analysis showed about the same carbon content in the silicon film as before. One must conclude a $10\text{\AA}$ SiO_2 layer was either not effective as a diffusion barrier or was evaporated during the outgassing process. More work needs to be done to find the efficiency of a SiO_2 layer as a diffusion barrier for carbon.

3. Coating Graphites with Glassy Carbon Layer

As recalled, among all the substrates studied, glassy carbon showed the least diffusion of carbon into the deposited silicon film and also the least silicon penetration into the substrate. Therefore, it would be desirable if one could either convert the graphite surface to glassy carbon or coat the graphite with some organic material and convert it to glassy carbon before silicon deposition. The latter process should be more practical and use can be made of the existing industrial process for manufacturing glassy carbon. For example, pyrolysis of polyfurfuryl alcohol at high temperature is used for this purpose.⁶ This possibility is presently under investigation.

DISCUSSION

A. Confirmation of High Diffusion Rates Observed

The observed high carbon content in the silicon films indicates a high diffusion rate of carbon into silicon at the temperature region of 1150°-1200°C, much higher than expected from published data on the bulk systems. Also, except for glassy carbon, silicon penetrated deeply into the carbon substrates. The high carbon content observed cannot be solely due to the ambient contamination at the vacuum of 1×10^{-6} Torr used in our studies. This is confirmed by the Auger analysis of the silicon film deposited onto quartz at room temperature. The carbon content was found to be less than 3 at.%. Analysis of the silicon film deposited onto quartz at 1150°-1200°C was unsuccessful because of the poor conductivity of the film.

Comparing the silicon films using carbon substrates, the silicon content inside the substrate is highest for the basal plane pyrolytic carbon, as is shown in Fig. 1. To confirm the high silicon content observed in the substrates the possible contribution of surface diffusion of silicon during sputtering was investigated. During the Auger analysis both the electron beam impact and Ar-ion sputtering could cause local heating and enhance lateral diffusion of surface silicon atoms to the spot being analyzed by the Auger beam. This possibility can be easily checked using the room temperature deposited silicon films. If the mentioned lateral diffusion of silicon is responsible for the observed high silicon content in the substrates, the same should also be observed for the room temperature deposited films. We, therefore, deposited 2000-3000Å thick silicon films on the edge plane and basal plane

pyrolytic graphite and extruded graphite, all kept at room temperature. All three Auger profiles have similar shapes and that of the basal plane is shown in Fig. 4. It is clear from Fig. 4 that the lateral diffusion described above is not responsible for the observed high silicon content of substrates onto which silicon was deposited at high temperature. This, therefore, confirms that the high silicon content inside the carbon substrates after high temperature silicon deposition is not an artifact.

B. Diffusion Mechanism

The formation of thin film silicon carbide has been reported when silicon is heated in high vacuum⁷⁻⁹ and upon chemical vapor deposition of carbon on silicon.^{7,10-12} The former is due to a reaction of silicon with the carbon-containing species in the ambient background, and the latter is proposed to be due to the diffusion of either carbon or silicon through the initially formed SiC film.^{11,12} Here we compare the chemical vapor deposition work of carbon on silicon with our study of silicon deposited on carbon. Nakashima et al.,¹¹ applying the theory of metal oxidation, concluded that carbon diffusion through the initially formed SiC was responsible for the SiC formation. Rai-Choudhury and Formigoni,¹² on the other hand, applying the extrapolated bulk diffusion data of silicon and carbon in SiC, concluded that silicon diffusion was the dominating factor for the SiC formation. As we mentioned earlier, thin film systems could be very different from the bulk. During evaporation and chemical vapor deposition, the vapor atoms arrive on the substrate surface in an unbound form. These atoms can, therefore, easily diffuse both laterally on the surface and into the

substrate. The diffusion coefficient can be much larger than that from the bulk where chemical bonds have to be broken before the atoms can diffuse. Other things being equal, the evaporated atoms should have a higher diffusion rate through some intermediate film than those from the substrate. In our studies we observed high content of both carbon in silicon and silicon in carbon. This indicated not only a high diffusion rate of silicon, but also a high diffusion rate of carbon into the silicon film from its bonded form in the substrate. This idea will later be used in explaining our proposed diffusion mechanism.

It is recalled that the silicon content observed in the carbon substrates depends on the carbon structure, as shown in Fig. 1. If one arranges the substrates according to the silicon content one finds: basal>edge>extruded>glassy. The same decreasing order also coincides with the degree of structural perfection for the last three substrates. In addition, the observed silicon to carbon ratio in the basal plane substrate is nearly constant with depth. For the other three substrates, this ratio decreases with increasing penetration depth of silicon into the substrate. Arranging the substrates according to steepness of decrease one finds again: edge<extruded<glassy. These facts suggest some unique diffusion process which depends largely on the substrate orientation used for the silicon deposition. In the following we propose a possible diffusion mechanism to explain the mentioned observations.

In order to make the proposed diffusion mechanism easily visualized we divide it into two stages:

(1) The silicon atoms from the vapor arrive on the carbon surface and form a layer of silicon carbide. For the basal plane, where each carbon atom is σ -bonded to three other carbon atoms in the plane, and leaves only the π -orbital to bind with silicon, this would change all the surface carbon atoms from sp^2 to sp^3 bonding and convert the planar graphitic structure into one with characteristic tetrahedral bonding. However, unlike the ordinary chain polymers where zigzag type of chain alignment is possible, the planar graphitic structure would now be under a rather strong distortion. Some C-C bonds have to break to release this distortion. In addition, the thermodynamically favored formation of new tetrahedral Si-Si bonds among the silicon atoms adds further distortion to this surface graphite layer. These factors combined would very likely crack the surface graphite layer into small carbon clusters each of which is bonded to some silicon atoms in the form described above.

For the edge plane, however, it can be easily seen that such cracking would take place less efficiently. Take a perfect edge plane for example. All the surface carbon atoms not shared by two neighboring hexagons have σ orbitals available in addition to the π -orbitals. Silicon atoms bonded to the former position, which make silicon coplanar with the graphite layer, are rather far from one another and bonding among them seems less likely. Silicon atoms bonded to the π -orbitals of the surface carbon atoms should show a similar effect as that described for the basal planes. However, this monolayer coverage of silicon atoms on the surface carbon layer could at most distort only the surface carbon and some nearest neighbor atoms. Diffusion of more silicon atoms into

the interplanar "channels" would be necessary before the first hexagon of each layer could be effectively distorted and cracked. The basal plane is, therefore, much more easily cracked than the edge plane.

(2) During or after the first stage described above, the later arriving silicon atoms from the vapor would either bond to the available silicon atoms or diffuse through the carbide layer into the substrate. The former process would tend to align the surface silicon atoms into a well ordered form. This could cause further cracking of the carbon clusters to attain a more stable configuration. The silicon atoms diffused into the substrate would bond to the first available carbon atom and repeat the process of stage 1.

According to this mechanism one expects a rather constant Si/C ratio deep into the substrate for the basal plane case. The above described cracking and diffusion processes would simply repeat themselves to nearly the same extent because of the high cracking efficiency and the uniform layer structure encountered. For the edge plane, the lower cracking efficiency, the necessary diffusion before each effective cracking, and the less uniformity in structure going into the substrate all contribute to a decreasing Si/C ratio with diffusion depth into the substrate. Also, the dominant role of cracking is in agreement with the observed lowest content of silicon in glassy carbon. Glassy carbon is known to contain a significant portion of sp^3 bonded carbon atoms.⁶ This certainly means much less distortion and, therefore, less cracking of the carbon lattice after the formation of a carbide layer. Silicon diffusion into the carbon lattice alone would probably be the dominant factor for most of the observed silicon content in glassy carbon. The

fact that very low silicon content was observed in glassy carbon indicates a rather low diffusion rate of silicon in this substrate.

The above proposed diffusion mechanism is shown to qualitatively explain the observations of this study. A quantitative test of the proposed mechanism requires the determination of diffusion constants on all the substrates over a wide temperature range. This is currently under study and will be reported later.

It is emphasized that although our proposed diffusion mechanism describes the silicon diffusion into the carbon substrates, the described exchange process also leaves some of the carbon atoms on or near the surface of the deposited silicon films. This explains our observed high carbon content immediately after the surface contamination is sputtered off. In our studies the silicon deposition rate is low, being ca $50\text{\AA}/\text{min}$, and high carbon content is observed throughout the silicon films deposited. For a very high deposition rate, e.g., a few microns per min, the deposition rate could exceed the diffusion rate. One might then obtain silicon films containing very small amounts of carbon in the bulk film, and large amount of carbon only at regions near the silicon-substrate interface. As described earlier in the text, silicon vapor atoms are expected to show a higher rate of diffusion than those from the bulk. The latter atoms will have to break some Si-Si bonds before they can exchange with the carbon atoms. Some experimental verification of this fact is already known⁴ and a more systematic study of this deposition rate dependence will be carried out later in this laboratory.

The observed formation of carbide in the deposited silicon film is in agreement with the proposed diffusion mechanism. However, the Auger peak shape of carbon seems to be dependent on the relative ratio of Si/C in both the silicon films and the carbon substrates analyzed. This can be seen from the mentioned exception, the basal plane graphite substrate. The high Si/C ratio observed in this substrate is accompanied by a persistent carbide Auger peak shape. In addition, Fig. 4 indicates a transition of carbon from carbide to graphitic form between a relative Si/C intensity ratio of ca 5 and 1. After correction for the intensity difference between silicon and carbon using bulk SiC as standard,¹³ this corresponds to a Si/C concentration ratio of ca 2.5 and 0.5, respectively. Further work indicates a transition point at a Si/C concentration ratio close to 0.5.¹⁴ More work is in progress to understand the physical basis of this observation.

CONCLUSION

We have studied the high temperature vacuum deposition of silicon thin films on the various forms of carbon. Auger spectroscopic study indicates a high diffusion rate of silicon and carbon into each other and the formation of SiC. It is shown that a diffusion barrier is needed to use the carbon as the substrate material in thin film silicon solar cells. Several attempts have been made to build a diffusion barrier and more work needs to be done to find an effective barrier for this purpose.

A diffusion mechanism is proposed according to which silicon atoms first form a carbide layer with the surface carbon atoms, followed by repeated cracking of the carbon lattice and diffusion of silicon through the carbide layers. This mechanism is shown to account for the observed dependence of the diffusion on the structure of the carbon substrates used. The effect of varying the deposition rate on this diffusion mechanism has also been discussed.

A similar diffusion mechanism might be used to explain the formation of SiC upon chemical vapor deposition of carbon on silicon. Here, the first layer of SiC could distort the silicon surface layer due to the tendency of C-C bond formation and mismatch between the two lattice constants. Some of the surface silicon bonds could break and allow more Si-C bonds to be formed between the surface silicon atoms and the diffused carbon atoms from the vapor. Again, the vapor atoms, in this case carbon, could diffuse through the SiC film more easily than the substrate atoms, here the silicon atoms, which are in the bound form. However, the above described distortion could also lead to cracking of

the silicon layer and produce less-bonded silicon atoms for an easier diffusion into the carbon region. An Auger analysis similar to the present work will be helpful to better understand this system.

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REFERENCES

1. R. I. Sapce and G. A. Slack, Proceedings of the Conference on Silicon Carbide, Boston, April, 1959. (Pergamon Press, 1960).
2. C.-A. Chang, W. J. Siekhaus, T. Kaminska and D. T. Huo, Appl. Phys. Lett. 26, 178 (1975).
3. T. W. Haas, J. T. Grant and G. J. Dooley III, J. Appl. Phys. 43, 1853 (1972).
4. T. L. Chu, private communication.
5. F. Lukes, Surface Science 30, 91 (1972).
6. D. W. McKee, Ann. Rev. Materials Science 3, 195 (1973).
7. I. H. Khan and R. N. Summergrad, Appl. Phys. Lett. 11, 12 (1967).
8. H. Poser, Z. Phys. Chem. 228, 113 (1965).
9. E. Biederman and K. Brack, J. Appl. Phys. 37, 4288 (1966).
10. W. G. Spitzer, D. A. Kleinman and C. J. Frosch, Phys. Rev. 113, (1959).
11. H. Nakashima, T. Sugaro and H. Yanai, Japan J. Appl. Phys. 5, 874 (1966).
12. P. Rai-Choudhury and N. P. Formigoni, J. Electrochem. Soc. 116, 1440 (1969).
13. Thomas Kaminska, private communication.
14. C.-A. Chang, unpublished results.

FIGURE CAPTIONS

- Fig. 1. Auger depth profiles for the high temperature (1150°-1200°C) deposited silicon films on (a) edge plane of pyrolytic graphite, (b) basal plane of pyrolytic graphite, (c) extruded graphite, and (d) glassy carbon.
- Fig. 2. Auger peak shapes of carbon observed during Ar-ion sputtering of the silicon film deposited on the edge plane of pyrolytic graphite. The three peaks shown correspond to the respective regions marked by arrows in Fig. 1a.
- Fig. 3. Auger depth profiles for the (room temperature plus high temperature) silicon films deposited on (a) edge plane of pyrolytic graphite, (b) basal plane of pyrolytic graphite, (c) extruded graphite, and (d) glassy carbon.
- Fig. 4. (a) Auger depth profile for the silicon film deposited on the basal plane of pyrolytic graphite at room temperature; (b) Auger peak shapes of carbon corresponding to the marked positions of (a).

Fig. 1a

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Fig. 1b

Fig. 1c

Fig. 1d

XBL 749-7321

Fig. 2

Fig. 3a

Fig. 3b

Fig. 3c

Fig. 3d

Fig. 4a

4 b

a

b

c

XBL 7410-7418

Fig. 4b

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