Conductivity and ESR Measurements on Carbon Rich Cathodic Amorphous Silicon Carbon Alloys

A. L. Baia Neto[1], F. Finger[2] and S. S. Camargo Jr[1]
[1]*Departamento de Engenharia Metalúrgica e de Materiais, Universidade Federal do Rio de Janeiro, Rio de Janeiro, Brazil*
[2]*ISI-PV, Forschungszentrum Jülich, Jülich, Germany*

Received July 21, 1995

The conductivity and ESR spectra of silicon incorporated a-C:H films deposited on the cathode of a glow discharge deposition system were studied. In case of as deposited samples the conductivity is strongly dependent on the silicon content of the films, as well as on thermal annealing. The analysis of the observed behavior indicates the presence of a density of deposition related defects which cannot be directly related to the silicon incorporation, but to the deposition process. ESR measurements show that sp^2 carbon clusters with an unpaired electron are the dominant type of defects for silicon contents of up to 40 at.%. It is observed that silicon incorporation induces a reduction in both the density and size of these clusters. The effect of thermal annealing on the ESR results of these samples is analyzed.

I. Introduction

The hydrogenated amorphous silicon carbon alloy system is a rather interesting one due to the large diversity of materials and properties that one may obtain when producing the films under the appropriate conditions. On the amorphous silicon side of this system, one generally deposits the films under relatively "soft" conditions and obtains a material with high electronic quality and commercial applications in solar cells and photoreceptors[1]. On the opposite side of this alloy system, one generally produces a-C:H under strong particle bombardment and obtains films that present high hardness and are suitable for mechanical applications[2,3].

Although carbon incorporation into a-Si: H has been extensively studied during the last several years, up to now very little attention was paid to the incorporation of silicon atoms into hard a-C:H films. Oguri and Arai obtained films with friction coefficients as low as 0.05 and showed that silicon incorporation tends to stabilize C-C sp^3 bonds[4,5]. De Michellis et al. obtained films by sputter-assisted plasma CVD, investigated their electronic properties and concluded that a reduction in the size of graphitic domains is induced by the incorporation of silicon atoms[6]. Accordingly, Smeets et al. showed that carbon rich samples deposited by plasma enhanced CVD have the diamond-like structure and obtained films with very low friction coefficients[7].

In this work, in order to investigate the influence of silicon incorporation on the electronic properties of diamond-like a-C:H films, we study the conductivity and ESR spectra of carbon rich silicon carbon alloys deposited the cathode of a RF glow discharge system. Thermal annealing experiments were done in order to investigate the stability of these films.

II. Experimental details

The films were deposited onto high resistivity crystalline silicon and Corning 7059 glass substrates placed on the cathode of a radio frequency plasma assisted CVD reactor, with no intentional heating. Gaseous mixtures of silane and methane, with silane contents ranging from zero to 15 vol.% were fed into the reactor through mass flow controllers. All of the samples were obtained using a self-bias voltage and chamber pressure of -200 V and 0.08 mbar, respectively. Under these conditions, the temperature of a crystalline silicon substrate was measured during deposition using a thermocouple pressed on its surface and found to be about

100°C. The thickness of the deposited films varied from 1 to 2 μm.

ESR measurements were taken in a commercial X-band spectrometer with a cylindrical TM cavity at room temperature. The magnetic filed was calibrated versus a secondary standard of sputtered amorphous silicon which was also used as spin density standard. Dark conductivity measurements were taken by gradually heating the sample from room temperature up to 500K in a conventional liquid nitrogen cryostat using coplanar aluminum electrodes of 1 cm width and 0.25 mm spacing.

III. Results and discussion

The results obtained for dark conductivity measurements as a function of temperature for as deposited samples with different silicon contents are shown in Fig. 1. As it can be seen, silicon incorporation increases the conductivity by orders of magnitude comparatively to that of pure a-C:H. In this case the observed behavior of $\sigma(T) = A\exp(-\beta/T^{1/4})$ indicates that variable range hopping is the main conduction mechanism, which is an evidence of the presence of a high density of defects. In case of the silicon incorporated samples, as the temperature is raised, the observed behavior deviates from the above mentioned one due to the fact that the sample is annealed during the conductivity measurements and, consequently, the conductivity is lowered.

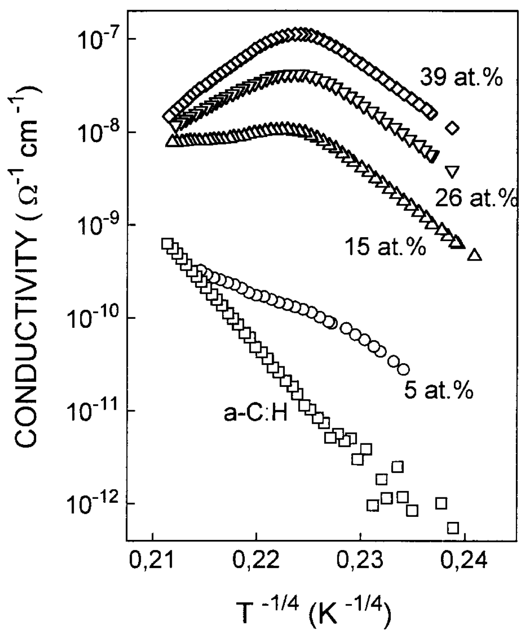

Figure 1. Dark conductivity as a function of temperature for as deposited samples.

Fig. 2 shows the conductivity results obtained for samples annealed at 200°C during 30 minutes in vacuum. In this case, variable range hopping is the conduction mechanism for all investigated samples. The comparison between the results of Figs. 1 and 2 shows that annealing induces a conductivity decrease of orders of magnitude in case of the silicon incorporated samples, indicating that structural rearrangements and a consequent defect decrease takes place. This decrease of the conductivity for samples annealed in this temperature range evidence the lower stability of silicon incorporated samples in comparison to pure a-C:H films. In fact, this behavior has already been observed in properties like internal stress and hydrogen content[8]. Additionally, one may observe that the conductivity of all annealed samples are similar to each other, suggesting that the conduction path is not affected much by the silicon content of the samples.

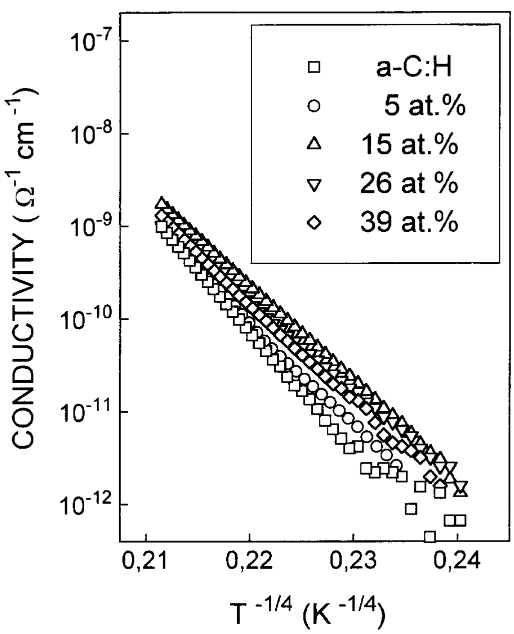

Figure 2. Dark conductivity as a function of temperature for samples annealed at 200°.

In order to understand the above results one may separate the total defect density of these films in basically two contributions: (i) carbon-type defects, which are basically those present in pure a-C:H, and are related to the presence of sp^2 carbon atoms and, (ii) deposition-related defects. When the samples are annealed at 200°C, carbon-type defects are not affected much, as one may observe by the comparison of the two conductivity curves for pure; C:H shown in Figs. 1 and 2. On the other hand, deposition-related defects are annealed out almost completely as suggested by the similarity of the conductivity curves for samples of different silicon contents, shown in Fig. 2. Therefore, these defects are not intrinsic to the material and we attribute their existence to changes in the deposition process caused by the presence silane in the discharge.

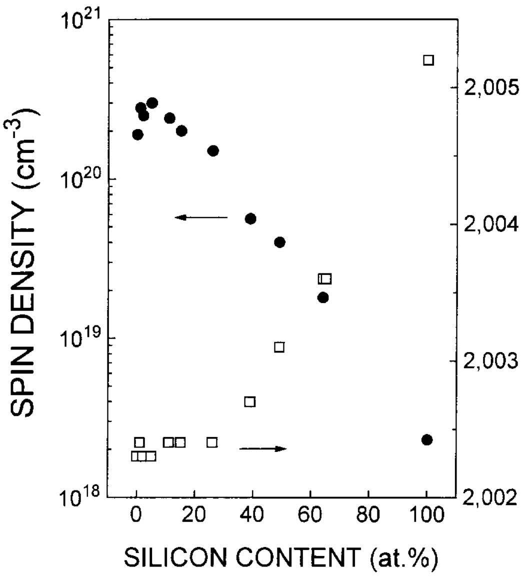

Figure 3. Spin density and g-value as a function of silicon content.

Fig. 3 shows the values of spin density (circles) and g-value (squares), obtained by ESR, as a function of the silicon content of the films. For low silicon content samples the spin density is very high and in good agreement with values previously reported for hard a-C:H films ($\sim 10^{20}$ cm^{-3}) [9]. As the silicon content is increased, the spin density initially increases slightly and for silicon concentrations larger than 5 at.% a strong decrease to values of the order of 10^{18} cm^{-3} is observed. The influence of silicon incorporation on g-value, reveals that for silicon contents up to 40 at.% the ESR signal is dominated by defects similar to those of pure a-C:H, and for silicon concentrations larger than 40 at.% the g-values increases towards the one usually observed for a-Si:H, indicating a predominance of silicon dangling bonds[10]. Assuming that graphitic clusters with odd number of π orbitals are responsible for the ESR signal of a-C:H films[3] one can conclude from these results that for concentrations lower than 40 at.%, the incorporation of silicon atoms does not appreciably change the dominant type of defects but does reduce their density. It should be pointed out that Raman spectroscopy results indicated a reduction in the sp^2/sp^3 fraction with silicon content[11].

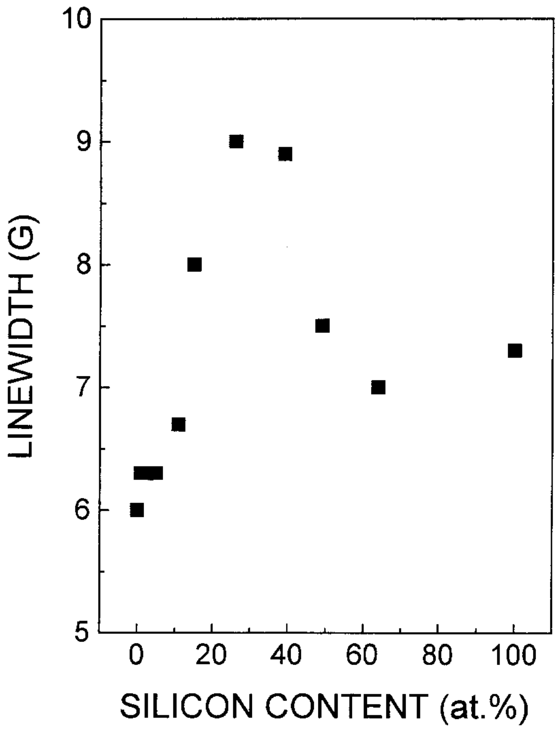

Figure 4. ESR signal linewidth as a function of silicon content.

In addition, an increase of ESR linewidth from 6 to 9 G is observed as the silicon content is increased from zero to 40 at.%, as shown in Fig. 4. For pure a-C:H films, Kleber et al. suggest that a reduction of the ESR linewidth can be associated with an increase of the mean sp^2 cluster size[12]. Schwa et al. obtained a maximum linewidth of 5,2 G for films produced as a pressure of $0,93\times10^{-3}$ mbar, which was suggested as an evidence for smaller graphitic cluster sizes[13]. Within this framework, the increase of ESR linewidth observed in the low silicon content range is an evidence that silicon incorporation contributes to the reduction of the size of graphitic domains.

The ESR spectra of all investigated samples were also measured for different annealing temperatures up to 400°C. A typical behavior of the spin density and g-value as a function of annealing temperature for all investigated samples can be observed in Fig. 5 in the case of a 39 at.% Si sample. As annealing temperature increases the g-value remains approximately constant whereas the spin density is reduced by up to about one order of magnitude. It is important to note that although conductivity measurements suggest that the total density of sp^2 carbon-type defects are not affected by thermal annealing at 200°C, ESR measurements show that the number of defects with spin is indeed reduced. This effect may be understood by considering that the graphitic clusters with an unpaired electron may be converted to spinless graphitic clusters as a result of bond reconstruction caused by thermal annealing.

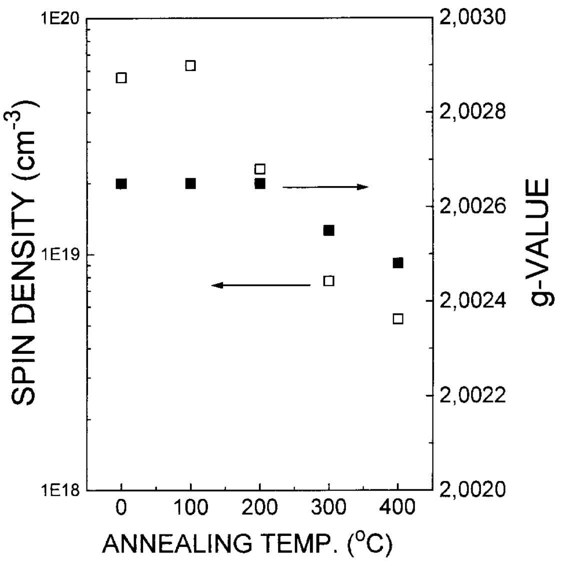

Figure 5. Spin density and g-value as a function of annealing temperature for a sample with silicon content of 39 at.%.

IV. Conclusions

The conductivity and ESR spectra of silicon incorporated a-C:H films were studied. Conductivity measurements indicated that the total density of defects may be separated into carbon-type defects and deposition related defects. The first group of defects is stable under thermal annealing at 200°C whereas the second group is annealed out almost completely, showing that they are not directly related to the silicon content of the films but due to changes in the deposition process.

ESR measurements showed that sp^2 carbon clusters with an unpaired electron are the dominant type of defects for silicon contents of up to 40 at.%. Silicon incorporation induces a reduction in the density and size of these clusters. Thermal annealing of the samples produced a decrease of the density of spins revealing that a conversion into spinless sp^2 carbon clusters occurs.

Acknowledgments

This work was supported by Finep and CNPq Brazilian agencies.

References

1. *Amorphous and microcrystalline semicondutor devices: optoelectronics devices* ed. by J. Kanicki (Artech House, Norwood, 1991).
2. J. C. Angus, P. Koidl and S. Domitz, in *Plasma Deposited Thin Films,* J. Mort and F. Jansen (eds.). CRC Press, Boca Raton, FL, 1986.
3. J. Robertson, Prog. Solid State Chemistry **21**, 199 (1991).
4. K. Oguri and T. Arai, J. Mater. Res. **5,** 2567 (1990).
5. K. Oguri and T. Arai, Thin Solid Films **208**, 158 (1992).
6. F. Demichelis, G. Giachello, C.F. Pirri and A. Tagliaferro, Proceedings of the 10th European Photovoltaic Solar Energy Conference, Lisbon, 1991, p. 125.
7. J. Smeets, J. Meneve, R. Jacobs, L. Eersels and E. Dekempeneer, J. de Physique IV, Coloque **C3**, 503 (1993).
8. A. L. Baia Neto, R. A. Santos, F. L. Freire and S. S. Camargo Jr., 8° Congresso Latino Americano de Ciências de Superfície e Aplicações, unpublished.
9. S. Schütte, S. Will, H. Mell and W. Fuhs, Diamond Rel. Mat. **2**, 1360 (1993).
10. M. Stutzmann, Z. Phys. Chem. **151**, 211 (1987).
11. A. L. Baia Neto, R. A. Santos, S. S. Camargo Jr., R. Carius, F. Finger and W. Beyer, Thin solid Films, unpublished.
12. R. Kleber, K. Jung, H. Ehrhardt I. Mühling, K. Breuer, H. Metz and F. Engelke, Thin Solid Films, **274**, 205(1991).
13. J. Schwam, S. Ulrich. K. Jung, H. Ehrhardt, R. Samlenski and R. Brenn Diamond and Rel. Mater., **304**, 4 (1995).