Amorphous Carbon Thin Films Deposited on Si and PET: Study of Interface States

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Thin carbon films with various thicknesses, deposited on different substrates (Si and poly-ethylene-terephthalate) at the same operating conditions in a radio frequency plasma enhanced chemical vapour deposition system were characterized by Doppler broadening spectroscopy. The films and the substrates were depth profiled by a slow positron beam. The aim of these measurements was to study the open volume structure and the interface of the films. It was found that, independently from the substrate, the films were homogeneous and exhibited the same open volume distribution. On the contrary, the effective positron diffusion length in the Si substrate was found to change with the thickness of the carbon films. This behaviour was interpreted as a change in the electric field at the carbon/silicon interface.

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1. Introduction

Diamond like carbon (DLC) films are intensively studied because of their many useful properties like chemical stability, biocompatibility, optical transparency in the visible range, high thermal conductivity, high electrical resistivity, and gas barrier capability. Their use is limited to few industrial niches (magnetic recording, wear protection, and antireflective coating) but now they are entering the field of biomedical, electronic application, and packaging.

Carbon films, deposited on (100) n-type Si and on poly-ethylene-
-terephthalate (PET), have been studied by positron annihilation spectroscopy

(PAS) in order to investigate the open volume distribution and interfacial states of the films deposited at the same conditions but having different thicknesses. There are few papers in literature dealing with PAS applied to study amorphous carbon films: investigation of their microscopic structure can be found in Ref. [1–4]. The open volume structure of these films is important because it affects their mechanical properties (hardness and stress). The interfacial states are fundamental for the adhesion of the films and for their possible use in electronic devices.

2. Experimental

The amorphous hydrogenated carbon (a-C:H) films were deposited on (100) n-type Si (3–25 Ω m resistivity) and on PET (10^{12} Ω m resistivity) at room temperature in a coupled radio frequency plasma enhanced chemical vapour deposition (RF-PECVD) system (13.56 MHz) using a mixture of CH_4-CO_2 (50% CO_2) as a gas precursor. In Fig. 1 a schematic drawing of the deposition system is presented. The cathode was the RF powered electrode ($V_{RF} = -300$ V), while the anode, where the substrate of the film was mounted, was without the application of any external bias (V_{BIAS}). With this experimental configuration the film grew at the floating potential given by the plasma. The deposition was carried out at a pressure of 0.2 Torr. The films were deposited on PET and on Si with the same time of deposition (from 780 s to 36×10^3 s). The obtained thicknesses of the films deposited on Si and PET were in the range between 9 ± 5 nm and 410 ± 100 nm, and 11 ± 2 nm and 500 ± 49 nm, respectively.
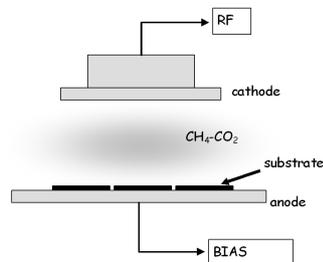
Fig. 1. Schematic representation of the coupled RF-PECVD system for the carbon film deposition.

Doppler broadening spectroscopy (DBS) was carried out with an electrostatic slow positron beam tunable in the 80 eV – 25 keV energy (E) range [5]. With these energies, a layer from 0.6 to about 3000 nm can be sampled. The mean positron implantation depth z is calculated according to the formula $z = (40/\rho) E^{1.6}$, with z in nm, while the density ρ and positron implantation energy E are expressed in grams per cubic centimetre and keV, respectively. The positron beam was coupled to a high purity Ge detector with a resolution of 1.2 keV at 511 keV. At each

positron implantation energy the 511 keV γ line was acquired with a microspectrum method and stabilized by a software procedure. The 511 keV annihilation line was characterized by the usual S parameter, defined as the ratio between the counts in a central area of the peak ($|511 - E_\gamma| \leq 0.85$ keV, in our experiment) and the counts in the total area of the peak ($|511 - E_\gamma| \leq 4.25$ keV). The S parameter represents the fraction of positron annihilating with low momentum electrons. The data of this multilayer system have been analyzed by the VEPFIT program [6].

The film thickness and the internal stress in the films deposited on Si were measured with a Kla Tencor P15 profilometer. In particular the determination of the stress was based on measuring radii of curvature of the wafers, after and before deposition, by means of the profilometer and using Stoney's equation [7].

3. Results and discussion

The measured S vs. E curves for a-C:H deposited on PET and a-C:H deposited on Si are shown in Fig. 2a and b, respectively. The films are denoted by their thickness as reported in the labels. The VEPFIT analysis indicates the presence of only two layers: the film and the substrate. In Fig. 2 we have not reported the fit lines for clarity: two examples for an a-C:H film deposited on PET and one deposited on Si are shown in Fig. 3. The position of the interface, as found by VEPFIT, is in good agreement with the thickness measured with the profilometer.
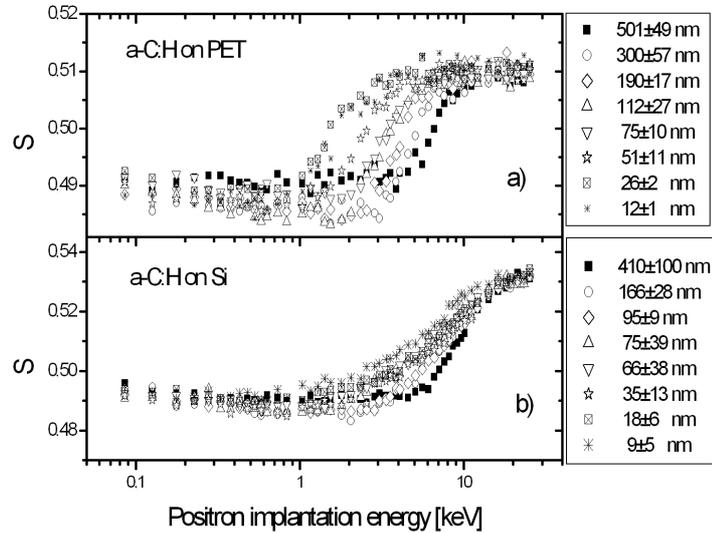
Fig. 2. $S(E)$ curves of the samples deposited on (a) PET, (b) Si.

The analysis of the data shows that the films, both grown on Si and on PET, are homogeneous as concerns the open volume distribution. In fact,
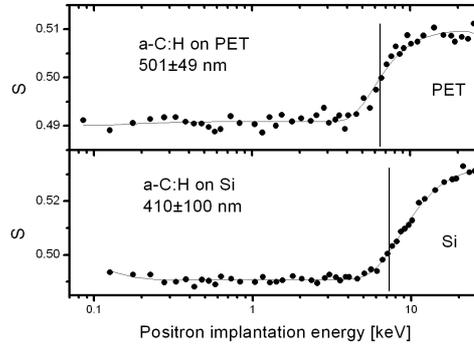
Fig. 3. Examples of the fit obtained by VEPFIT (continuous lines) of the $S(E)$ curves for the two relatively thick films. The vertical lines mark the film-substrate boundary.

the values of the film S parameter are found to be in the narrow ranges of $0.487 \div 0.491$ and of $0.484 \div 0.491$, for the samples on Si and on PET, respectively. The positron diffusion length in a-C:H is very low, about 1 nm, and this suggests that positrons are all trapped in the open volumes of the amorphous film. The agreement among the S parameter values of the different films indicates that the open volume structure is the same for all the films despite the different substrates and the different growing times.

As for the interfacial states, it is interesting to note that the positron diffusion length in (100) n-type Si was found to be 347 ± 8 nm before the film's deposition. A diffusion length higher than 200 nm [8, 9] is due to the presence of an electric field on the surface that attracts thermalised positrons. After the grown of the films, the diffusion length was found to be different and ranges between 242 ± 4 nm and 527 ± 13 nm when going from the 410 nm to 18 nm film thickness.

We explain this fact as a modification of the electric field at the a-C:H/Si interface due to the film deposition. Two possible mechanisms are supposed: a change in the band bending at the surface due to the induced stresses and/or a change in the charge states of the surface due to a mixing of C with the SiO_2 native oxide (1–2 nm) on the Si surface [10]. This second hypothesis, that also supposes the formation of new chemical bonds, is supported also by the fitting procedure that does not necessitate an interface layer in the description of the system.

In n doped Si, some surface levels are below the Fermi energy (E_F) and electrons may fill these surface states. This surface charge ($N_S e$) causes a depletion of electrons near the surface and it induces the electric field in the semiconductor [11]. In the simple model used here, the surface charge ($N_S e$) induces a depletion, of length d, created of homogeneous charge density ($N_d e$), such that $N_S = d N_d$. Using the Poisson equation, the electric field results in $E = -\frac{e N_d}{\varepsilon}(d - x)$, where x is the depth in the sample and N_d is the dopant concentration.

In the analysis with VEPFIT, the electric field linear dependence on the depth, was simulated by assuming boxes with decreasing E by assuming the same

total $E \times d$ area. The diffusion length in Si was assumed 200 nm as obtained by comparing n-type and p-type silicon [9]. From the fit procedure the values of the electric fields and the depletion layers in each sample were obtained.
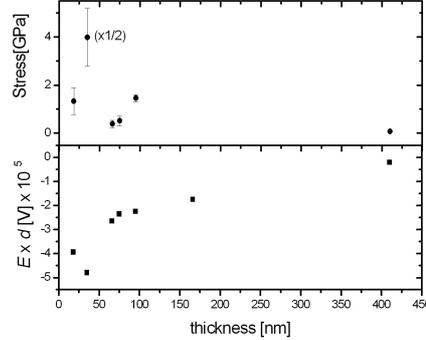
Fig. 4. The electric field times depletion depth ($E \times d$) induced by carbon deposition and the stress as a function of the film thickness. For clarity of presentation, the stress value at 35 nm film thickness was multiplied by 0.5. The errors for $E \times d$ are inside the points.

In Fig. 4 the stress and the product of the intensity of the electric field E and the depletion layer d are plotted as a function of the film thickness. The measured data point out that the magnitude of product of the intensity of the field and the width of the depletion layer increase when the thickness of the deposited films decreases. The stress data do not show a clear correlation with $E \times d$, and no conclusion can be drawn about a possible influence of the stress on E. It seems more plausible that these modifications are due to the intermixing of the first layer of the films and of the substrate with the introduction of different electronic defects. The intermixing caused by the ions impinging energy and substrate temperature, can produce a few layers with C–O, C–Si bonds, O related defects, and vacancies. Using the simple model of the surface electric field previously introduced, the surface negative charge have been estimated to range between 6×10^{12} and 9×10^{13} cm^{-2}.

4. Conclusions

Carbon films, deposited on (100) Si wafers and PET by PECVD, have been analyzed by PAS. The data show that the different type of substrate (Si and PET) and the different growing times of the film do not affect the open volume distribution: the films are homogeneous as probed by positrons (equal S parameters). VEPFIT analysis shows that the interface is sharp. Moreover, the fits show that the growth of the films modifies the electric field at the a-C:H/Si interface. It is not completely clear whether this modification is induced by stress, that modifies

the band bending, and/or from the first film layer that mixes C with Si and SiO$_2$ of the substrate first layers. More measurements and different analytical techniques are needed to clarify the observed phenomena.

Acknowledgments

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