

Stress and interfacial defects induced by amorphous carbon film growth on silicon

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Abstract

Amorphous hydrogenated carbon (*a*-C:H) films deposited on silicon substrate were characterized by positron annihilation spectroscopy (PAS) and mechanical measurements with the aim of studying the possible relations existing between the residual intrinsic stress and the distribution of open-volume defects in the films and at the film–substrate interface.

The carbon thin films were deposited by graphite sputtering in a RF Ar–H₂ plasma. Internal stress in films deposited with different thickness was measured in order to follow the film growth process and the induced mechanical effects in the films.

PAS measurements were carried out with a slow positron beam coupled to a high purity Ge detector to record the Doppler broadening of the positron–electron annihilation line as a function of the positron implantation depth. The positron data have been analysed by the stationary diffusion equation to extract the main information about the open volume depth distribution in the films and in the film–Si interface.

It was found that the films were homogeneous over all their thickness and presented an equal distribution of open-volumes whatever the thickness value. On the contrary, the growth process was accompanied by a strong modification at the film–Si interface. Here, the formation of a defected region, extending deeply in the Si, was found in all the samples. The region is more marked and more extended in depth in the thinnest and the thickest films, which on the other hand contained the highest compressive stress levels. The defects were identified as divacancy-like defects. The strong correlation between induced defects in the substrate and the stress is discussed.

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1. Introduction

a-C:H films exhibit a wide range of properties based on the variety of possible local environments, lying on the combination of sp² and sp³ hybridised carbon atoms in a disordered network. Interestingly, as the hydrogen content is increased, the films become more diamond-like with a higher degree of tetrahedral sp³ bonding, many of which terminated by hydrogen; conversely the films become softer and their hardness decreases. The increase of hydrogen

content produces also a relatively open structure that gives origin to less dense films. One drawback in the use of *a*-C:H films is due to the high compressive stress developed during their deposition. Several works report about high compressive stresses found in amorphous carbon (*a*-C) and *a*-C:H film deposited by different methods [1–4]. In many cases, these stresses are expected to affect the adhesion of *a*-C:H films to the substrate and to cause delamination and buckling of the films. When the adhesion is excellent and the compressive stress in the film exceeds the tensile stress in the substrate, failure will occur in the bulk material [1]. The internal stress in *a*-C:H films and the factors affecting it are still under study. It has been shown that the internal stress can be influenced by deposition parameters (such as

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gas pressure, source-to-substrate distance, substrate temperature and heat treatments) to the extent that stress variation from tensile to compressive is even possible [2,3]. In addition, it has been found that the internal stress in *a*-C:H and *a*-C films varies monotonically with sp^3 content and that it also depends on film thickness and growth process [4,5]. Many efforts have been devoted to produce less stressed carbon films without reducing the sp^3 fraction [6].

Stress relaxation mechanisms in carbon films deposited on Si are of different nature. Cheng et al. [3] have found that the decrease of the H content and the increase of sp^3/sp^2 ratio are the main factors that cause the reduction of internal stresses in an *a*-C:H film deposited by PECVD whereas, in addition to the above two factors, the incorporation of nitrogen atoms and the increase of void density can contribute to reduce the internal stress in *a*-C:H(N) films deposited by PECVD [7]. Also Freire et al. [8] pointed out that voids in *a*-C:H(N) films permit film relaxation. Puchert et al. [9] proposed a structure model in which voids are the most likely stress relief mechanism in sputtered *a*-C:H films. On the other hand, Kelires et al. [10], studying the growth process of an *a*-C film, concluded that interdiffusion at the film/substrate interface and stress relaxation are closely associated in the early stages of growth. Heiman et al. [11] have characterized, with transmission electron microscopy (TEM) and X ray diffraction (XRD), nanocrystalline carbon films deposited by DC glow discharge CVD at a temperature of 880 °C. They observed the presence of several defects at the interface and a highly dislocated Si substrate for more than 100 nm from the interface. The dislocation and interfacial defects formation was ascribed to the need of the structure to relax the thermal component of the stress.

In this work, with the aim of investigating the relation existing between open volumes, other defects and stresses, we have employed positron annihilation spectroscopy (PAS) to study (a) the open volume structure and (b) the interfacial and/or the sub interfacial point defects, in *a*-C:H films. The films were deposited by the sputtering technique fixing the depositions parameters and varying the deposition times. Stress measurements were correlated with PAS measurements.

2. Experimental

2.1. Film deposition

The films were sputter-deposited on n-type Si(100) (3–25 Ω m resistivity) wafers in a 84% Ar–16% H₂ discharge at 5 Pa pressure with a constant DC self-bias on the cathode of –550 V. The total gas flux was 30 sccm. A graphite target was used to grow the films. The samples were mounted on a rotating support, at a distance of 8 cm from the cathode and without application of any external bias. The films grew at

the floating potential given by the plasma, measured as 17 eV by means of a Langmuir probe. By the same, plasma potential was of 30 eV, which corresponds to a maximum ion energy bombardment of the growing film of 13 eV.

Both the cathode and the sample holder were water-cooled to room temperature. A series of samples were prepared with deposition times ranging from 4 to 164 min, hence for various thicknesses, ranging from 11 to 210 nm (nine samples).

2.2. Film characterization

The film thickness and the internal stress 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.

To gain information on the C bonds in the deposited films, the thickest film (210 nm thick) was characterized by Fourier-transform infrared spectroscopy (FTIR) using a Bio-Rad FTS 185 spectrometer equipped with a DTGS detector and a KBr beam splitter. The analysis was carried out in the wavenumber range of 400–4000 cm⁻¹. In particular, the 2600–3200 cm⁻¹ interval, corresponding to the stretching vibration modes of various C–H bonds, was considered [12,13]. The spectrum is shown in Fig. 1. It was deconvoluted, after a linear background subtraction, into individual peaks representing the specific stretching modes, namely: sp^3 -CH, sp^3 -CH₂, sp^3 -CH₃, olefinic sp^2 -CH, olefinic sp^2 -CH₂ and aromatic sp^2 -CH. Whenever the modes are symmetric (sym.) or anti-symmetric (asym.) is indicated in the figure. The films are best described as hydrogenated C ones. The small peak at 2826 cm⁻¹ in the spectrum may stem from methoxy-like bonds, more likely due to film oxygen contamination.

2.3. PAS measurements

PAS was carried out with an electrostatic slow positron beam tuneable in the 80 eV–25 keV energy (*E*) range [14].

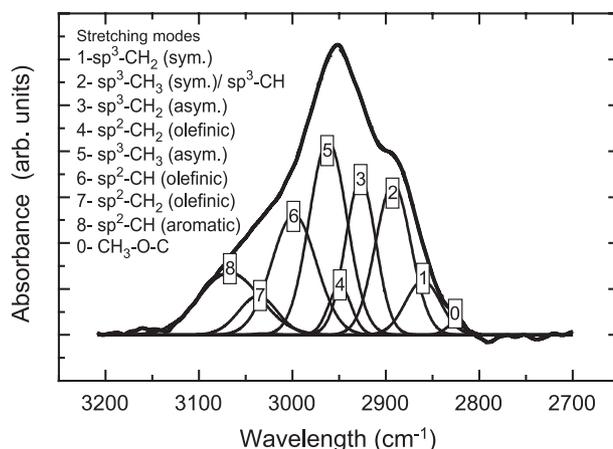


Fig. 1. A typical C–H stretch absorption spectrum for the films under study.

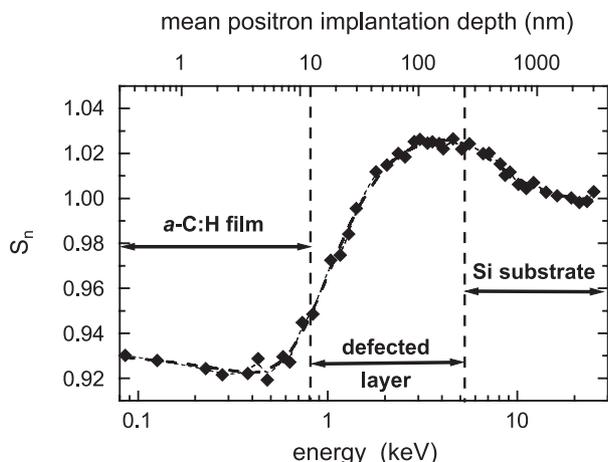


Fig. 2. Positron annihilation with low momentum electrons (S_n) versus positron implantation energy for the 11-nm-thick film. The mean positron implantation depth is reported on the upper scale.

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 when the density ρ and positron implantation energy E are expressed in g/cm^3 and keV, respectively [15]. 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 gamma line was acquired with a microspectrometry method and stabilized by a software procedure [16].

Positrons injected in a solid reach thermal energies in few picoseconds, then after a diffusion path are efficiently trapped in open structures, where present, and there annihilate with an electron. The high specific trapping rate of positrons for open volumes makes this particle a very efficient non-destructive probe for characterizing open volume defects from single vacancies to voids and porosities. The positron probe is sensitive to vacancy concentrations smaller than 1 ppm of vacancies. The annihilation characteristics are determined by the local electronic environment of the annihilation site.

We have analysed the Doppler broadening of the 511-keV annihilation line to extract information about the distribution of open volumes in the different layers of the samples [15]. The 511-keV annihilation line is usually characterized by the S parameter normalized to the Si bulk (substrate) value S_b ($S_n=S/S_b$) [15]. The 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), represents the fraction of positron annihilating with low momentum electrons.

The S_n value increases when positrons annihilate in open volume defects. The open volume depth profile of the studied samples can be described by the analysis of the S_n vs. E (depth) curves.

3. Results and discussion

In order to illustrate the PAS measurements, in Fig. 2, only the S_n vs. E (z : mean positron implantation depth) curve corresponding to the thinner sample is shown. The upper scale in Fig. 2 reports the mean positron implantation depth evaluated according above-mentioned relation, with the film density ranging from 1.9 to 2.2 g/cm^3 , depending on film thickness. The line through the experimental points was obtained by a fitting procedure (VEPFIT program) [17] based on the solution of the stationary positron diffusion equation. In all investigated samples, the experimental data were satisfactorily fitted assuming a structure of three layers each of them ascribed to a different positron annihilation sites: the a -C:H film, an intermediate layer and a semi-infinite Si bulk layer. The layer structure obtained for the thinner sample is also shown in Fig. 2. Basically, the information extracted from the fitting procedure, are the depth and the S_n characteristic value for each layer. In Fig. 3, the layered structure of the nine analysed samples, as obtained from the fitting procedure, is reported. In the same figure, the film thickness measured with the profilometer is also shown.

Before deposition, the Si substrate was characterized with PAS showing, from positrons point of view, a perfect crystal without defects.

The main information drawn from the fitting procedure is that the S_n parameter values obtained for the first layer, corresponding to the film, are almost constant in the nine samples: $S_n=0.913$. The constant S_n value indicates that the films are homogeneous and present an equal distribution of open-volumes whatever the thickness. Also the thickness

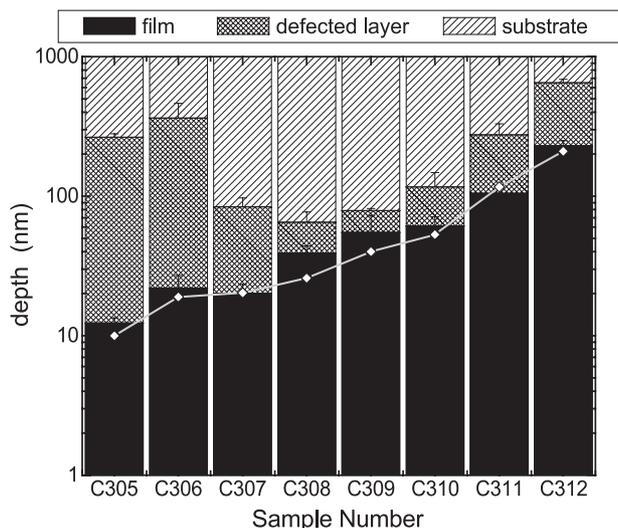


Fig. 3. Layered structure of the a -C:H films as obtained by fitting the PAS measurements. First layer: carbon film, second layer: defected layer of the Si substrate, third layer: undefected Si substrate. The white diamonds indicate the thickness of the films as measured with profilometer.

value obtained by the fitting procedure show a good agreement with the profilometer measurements (seen in Fig. 3). In the second layer, the fitted S_n parameter reaches a value higher than 1 ($S_n=1.03$), a strong indication of the presence of defects (see also the bump in the S_n curve in Fig. 2). This second layer is a defected layer in the Si substrate that extends deeply into the Si. Its thickness, ranging from ~ 20 to 400 nm, shows a non-monotonic behaviour with film thickness (Figs. 3 and 4b).

The $S_n=1.03$ value, found for the defective layer, is characteristics of defects with open volumes similar to divacancy in Si stabilized by extended defects or decorated by impurities [16].

The measured internal stress of the a-C:H films are shown in Fig. 4(a) as a function of the increasing thickness. In the figure, negative values of stress indicate compressive stress into the films. The graph shows that compressive stress has a significant dependence on film thickness. The first deposited layers cause a strong deformation of the Si wafer leading to a stress value of ~ 4 GPa and the sequentially deposited layers lead to stress relaxation. The stress reduction is observed up to ~ 50 nm where the stress reaches the minimum value of 0.13 GPa. Above this thickness, the compressive internal stress increases slowly. Analogous behaviours have been observed on a sputtered a-C:H films deposited on Si [8] with similar thickness, but in that case, the stress reaches a constant value above a critical film thickness and that type of behaviour was assigned to a stress relaxation mechanism based on void formation. It is worth noting that the defective layer as probed by PAS is thicker in the samples showing higher stress (compare Fig. 4a with b).

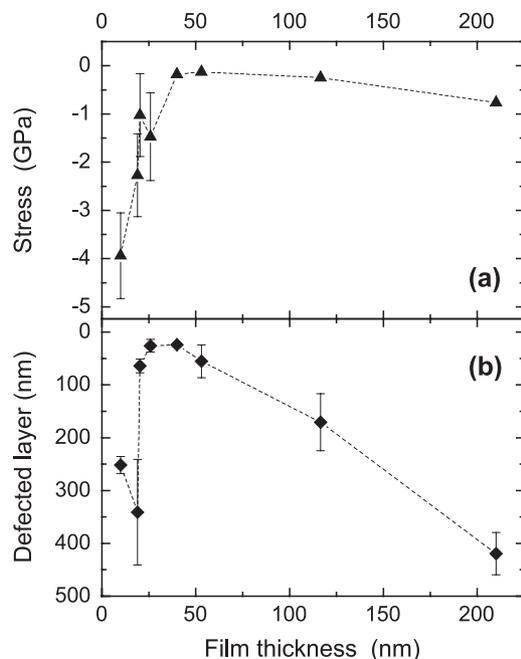


Fig. 4. (a) Compressive stress of the films and (b) depth of the defected layer in the Si substrate, as a function of the film thickness.

The present PAS measurements clearly point out that the films of our samples are all characterized by a homogeneous distribution of open volumes of the same nature independently from the thickness values of the films. As a consequence, we cannot invoke a different concentration or not uniform distribution of open volume in the film for explaining the different stress relaxation with the different thickness. At the contrary, it seems that part of the stress relaxes by creating defects in the substrate (Figs. 2 and 3).

The vacancy-like defects, observed by PAS in the substrate, extend too deeply to be originated by the creation of Frenkel pair due to the ion bombardment during the growing of the films. The projected penetration ranges for the energies, that ions like Ar^+ and the hydrogenic ones (H^+ , H_2^+ and H_3^+) in the plasma can gain by crossing the sheath towards the film, are respectively of ~ 0.3 and ~ 0.4 nm only. The more sounding explanation is that, during the growing of the film, the stress relaxes partially by inducing the formation of dislocations that move deeply in the substrate. Positrons probe indirectly the presence of dislocation being efficiently trapped in the vacancies incorporated in the dislocation core and vacancy formed and stabilized at jogs and kinks [18,19]. Vacancies produced during dislocations formation and movement can easily agglomerate to clusters [18] and it cannot be excluded that also the oxygen present in the Si crystal could be gettered at such defects, decorating partially the clusters [20].

Our results and the above consideration show that the defects created in the Si substrate during growing of the a-C:H film can play an important role in relaxing part of the intrinsic compressive stress and must be take into account besides other factors like: (a) the open volumes in the films [11]; (b) the intermixing and the vacancy formation in the film/substrate layer [10]; (c) the sp^3/sp^2 ratio [7]; (d) the transferred energy from the impinging ions [21].

4. Conclusions

We have found by PAS that stressed PVD a-C:H films present a defected layer in the silicon substrate. The thickness of these layers is directly related to the values of the residual stress in the films. The defects have been identified as defects with open volumes similar to divacancy that we have proposed to be stabilized by dislocations produced in the Si substrate. These defects are probably formed to relax part of the intrinsic compressive stress during the growing of the films.

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