Amorphous carbon film growth on Si: Correlation between stress and generation of defects into the substrate

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Amorphous carbon films of several thicknesses were prepared by graphite sputtering on crystalline silicon substrate. The samples were depth profiled with positron annihilation spectroscopy for open-volume measurements and characterized for their residual internal stress. It was found that after film growth the substrate presents vacancy-like defects decorated by oxygen in a layer extending in the substrate by several tens of nanometers beyond the film/Si interface. The width of the defected layer and the decoration of vacancy-like defects are directly and inversely proportional to the measured intensity of the residual stress, respectively. These findings indicate the existence of a relaxation mechanism of the stress in the films that involves deeply the substrate. The decorated vacancy-like defects are suggested to be bounded to dislocations induced in the substrate by the stress relaxation. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1940738]

Diamond-like carbon (DLC) materials due to their unique mechanical, chemical, electrical, and optical properties are widely studied and find many applications in several fields, from biomedical to microelectronics.[1] Their growth mechanisms have been deeply investigated[1] and better understood than stress generation and stress relaxation mechanism[2–8] which accompany the film formation. Many factors affect the stress generation, like deposition parameters, growth process,[2,5] the sp^3-hybridized carbon versus the sp^2-one content ratio,[4,5] and structural defects in the film. The compressive stress in DLC films was found to be inversely proportional to the films thickness[3,8] and the relaxation mechanisms to be strongly related to the rearrangement of carbon network,[7] to the defects (voids, vacancies) present into the film[3,5,6] and to the interdiffusion at the film/substrate interface.[8] No investigations have been done about the occurrence of relaxation processes involving the substrate itself. In this letter we will show that a specific relaxation mechanism can act inside the substrate over depths well beyond those expected if the process would only concern an interdiffusion at the film/substrate interface. It was found by depth profiling with positron annihilation spectroscopy (DP–PAS), a powerful technique for detecting defects from single vacancies to voids,[9] that the stress during the growth of carbon films also produces decorated defects in Si substrate that could contribute to the film stress relaxation. These defects, in an unexpected way, extend deeply in the Si substrate. Moreover we have found that in some cases these defects are produced in nonequilibrium, and evolve in time, probably inducing also a further relaxation of the film stress.

The studied carbon films were sputter deposited from a graphite target on n-type Si (100) (3–25 Ω m resistivity, 14.5 ppm of oxygen content) wafers in a Ar (84%)–H_2 (16%) radio-frequency discharge at 5 Pa pressure, for a total gas flux of 30 sccm, with a constant dc self-bias voltage of −550 V on the cathode. 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 V by means of a Langmuir probe. By the same, plasma potential was of 30 V, 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 with thickness ranging from 11 to 210 nm (8 samples, numbered Nos. 1–8 from the thinnest to the thickest one) was prepared by changing only the deposition time.

The C films (see Ref. 10) have been characterized both from a chemical and mechanical point of view by Fourier-transform infrared (FTIR) spectroscopy and nanoindentation measurements, respectively. In the latter case, a CSM instrument, equipped with a pyramidal (Berkovitch) diamond tip was used. The obtained films are best described as *a*-C:H films (hydrogenated amorphous carbon films) with a nanohardness of ~7 GP. The width of the film/substrate interface, where intermixing of C, O, and Si takes place, was determined by means of Auger electron spectroscopy depth profiling.

A 120-nm-thick, unhydrogenated (*a*-C) film with ~16 GP nanohardness, was deposited but with a pure Ar plasma to check if H plays any role in the defect generation and decoration in the substrate.

The film thickness and their curvature were measured with a Kla Tencor P15 profilometer. The radii of curvature of the wafers were measured before and after deposition (R_0 and R, respectively) and the stress (σ) in the films calculated using Stoney's equation: $\sigma=(1/t_f)[E_y t_s^2/6(1-\nu)](1/R-1/R_0)$, where t_f and t_s are the thickness of the film and of the substrate, respectively, E_y is the Young's modulus, and ν the Poisson coefficient of the substrate.

PAS measurements were performed with an electrostatic slow positron beam (positron implantation energy E in the 0.06–25 keV energy range)[11] (i) in DP–PAS for defect detections, using the Doppler broadening spectroscopy (DBS) and (ii) for the defect chemical environment characterization, by

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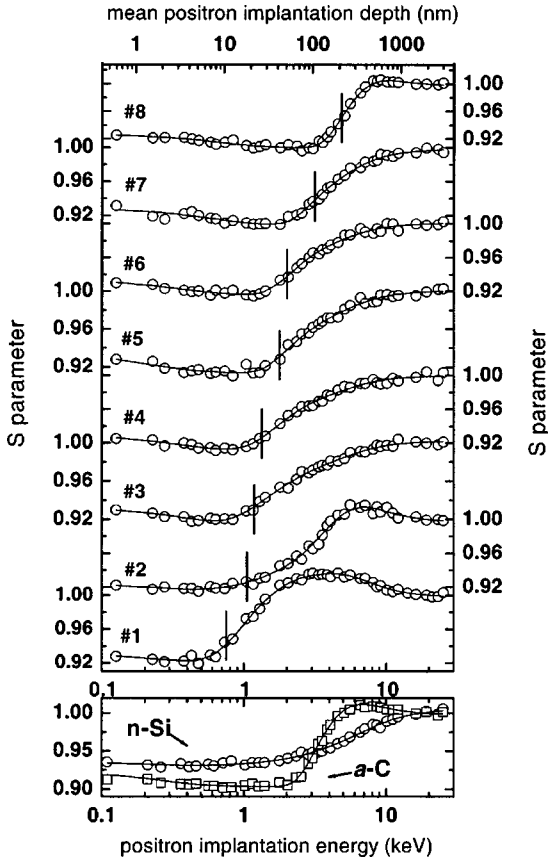

FIG. 1. S_n vs positron implantation energy, and mean positron implantation depth, for *n*-type Si (100), *a*-C film grown on Si, and *a*-C:H films grown on Si with increasing thickness (Nos. 1–8 samples set). S_n scale is reported on the left and on the right for odd and even samples, respectively. The interfaces are marked with a vertical line. The continuous line is the best fit based on the positron diffusion equation.

applying DBS in coincidence mode.[9] The mean positron implantation depth $\overline{z}$ is related to E according to the formula $\overline{z}=(40/\rho)\ E^{1.6}$, with $\overline{z}$ in nm when the density ρ and E are expressed in g/cm^3 and keV, respectively. The 511 keV Doppler broadened annihilation line was acquired with a high purity Ge detector (HPGe) (1.2 keV resolution at 511 keV) at several E. The 511 keV line was characterized with the shape parameter S calculated as the ratio of the counts in the central area of the peak ($|511-E_\gamma|\leqslant 0.85$ keV) to the total area of the peak ($|511-E_\gamma|\leqslant 4.25$ keV) and with the wing parameter W that is the fraction of the counts in the wing region ($1.6 \leqslant |511-E_\gamma| \leqslant 4$ keV). The S, W parameters were normalized to the Si bulk value $S_b(S_n=S/S_b)$, $W_b(W_n=W/W_b)$. The S_n, W_n versus energy (depth) curves have been fitted by the VEPFIT program based on the solution of the stationary positron diffusion equation[12] to extract the characteristics S and W values of the defects in the substrate (S_d, W_d) and in the C films (S_f, W_f). In order to match the film thicknesses measured by profilometry, a value of 1.98 ± 0.05 g/cm^3 for the film density was used. The DBS in coincidence[13,14] measurements were made with two low noise HPGe detectors placed at 180° (45% efficiency, 1.4 keV resolutions at 511 keV).

Coming now to the results, it turns out, from the depth-profiling analysis, that the S_n vs E and W_n vs E curves are well fitted with three layers: the film, followed by a defective layer and then by the unaltered Si substrate. The result will be discussed with reference to the S_n vs E data for the *a*-C:H, *a*-C samples, and the *n*-Si (100) used as substrate (see Fig. 1). The S_n data for *n*-Si (100) are fitted with a monotonic curve (positron diffusion length $L_+=249$ nm) increasing from an $S=0.928$ at the surface to the S_b value; this shows that the substrate is undefected before deposition of the films. At the contrary the *a*-C:H samples with the less and the more thick films (namely Nos. 1, 2, 8) clearly exhibit (Fig. 1) an increase of the S parameter in the depth region beyond the film/Si interface, which indicates the presence of open volume defects. The fitted (S_d, W_d) values equal to (1.028, 0.883), (1.028, 0.883), (1.04, 0.872), respectively, are typical of mono- and divacancies in Si decorated by impurities. Where not stated the errors on S and W values are 1×10^{-3}, 2×10^{-3}, respectively. Also the *a*-C film presents an evident defective layer with $(S_d, W_d)=(1.03, 0.873\pm0.008)$. The (S_d, W_d) in the defective layer of Nos. 3–7 samples was found to be $(0.967\pm0.002, 1.105\pm0.008)$. L_+, in the Si defective layer of all samples, drops to the very low value of 13.6 ± 2.5 nm, pointing out a strong positron trapping by defects. We stress that the presence of an electric field at the film/substrate interface, if ever,[15] is masked by the high trapping in the defected layer (low effective L_+), moreover an artificial introduction of a field was tested to cause the inconsistence of the fitting procedure.

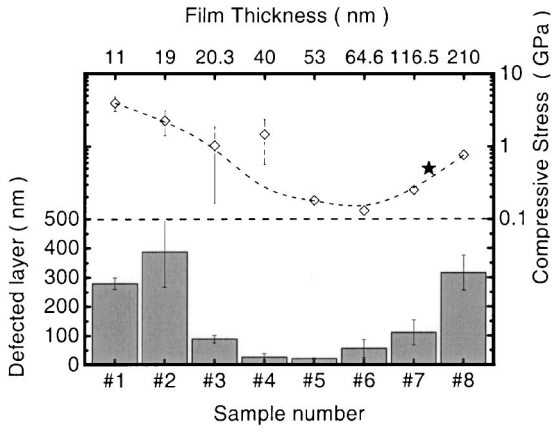

FIG. 2. Width of the defective layer in the Si substrate beyond the carbon film/Si interface, and compressive stress for the Nos. 1–8 *a*-C:H samples set. Full star: stress for 120-nm-thick *a*-C film.

The *a*-C:H films were found to be homogeneous, with the same (S_f, W_f) values $(0.913\pm0.001, 1.301\pm0.0012)$, and the same L_+ $(5.5\pm1.1$ nm). The $S_f=0.903$, $W_f=1.362$ and $L_+=2$ nm found values in the *a*-C film point out a structure with smaller open volumes in comparison with the *a*-C:H films.

The width of the defective layer in the substrate and the stress of the *a*-C:H films are reported in Fig. 2. There is a fine correlation between these two parameters: the defective layer is larger in the samples with the higher stress. In the same manner, the stress (star in Fig. 2) and the width (160 nm) of the defective layer in the unhydrogenated *a*-C film are also correlated, just as in the *a*-C:H films, which points out that hydrogen is not directly implied in the defective layer formation.

On the other hand, the S_d values were found to decrease (and conversely the W_d to increase) with the aging time in the samples with the highest residual stress. Figure 3 shows the S_n, values versus E for the Nos. 1, 6, and 8 samples, obtained from measurements made at two different times:

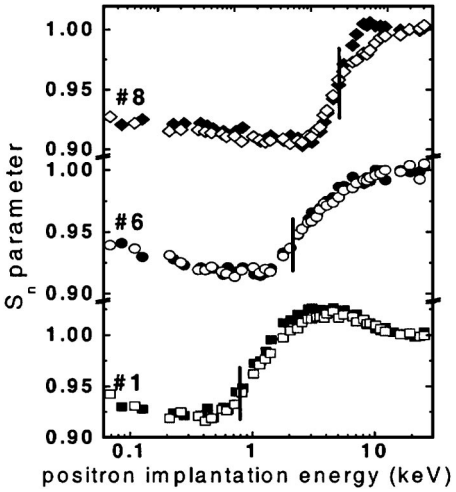

FIG. 3. S_n vs positron implantation energy for Nos. 1, 6, 8 *a*-C:H samples. Full symbols: measured on freshly deposited samples; open symbols: after 2 years aging. The interface is marked with a vertical line.

just after film deposition and after two years aging time in atmosphere. The decrease of S_n in the Nos. 1 and 8, after aging, is evident in the defected layer beyond the interface. In these two samples, the S_d values from the fitting procedure have been found to decrease, respectively, to 1.023 and 0.99 (from an initial value of 1.028 and 1.04).

The defects decoration is confirmed and highlighted by DBS in coincidence measurements. These measurements are usually presented as ratio curves with a reference curve (in our case a curve measured in bulk Si).[13] The characteristic ratio curve of positron annihilating into defects can be obtained[14] by measuring the ratio curve in bulk Si, in the film and in the centre of the defective layer, and knowing the positron fraction of positron annihilating into the bulk, the film and in the defective layer at each positron implantation energy. We have extracted these fractions by the SWAN program[16] using as input the *S*, *W* couples of the different states obtained by the VEPFIT program and reported earlier. The characteristic ratio curves of positron annihilating in the defects after ageing are presented in Fig. 4 for sample Nos. 1, 6, 8, and *a*-C. Previous works showed that carbon and oxygen give characteristic peaks in the ratio curves with Si, both around 514 keV. As during the film growth, the C intermixing with Si is only confined to 8–9 nm (as measured by Auger spectroscopy depth profiling), we can attribute the peaks in Fig. 4 to positron annihilating with high momentum electrons of oxygen atoms.[17,18] The ratio curves of sample Nos. 3–7 and sample Nos. 1 and 2 are practically equal, within the error bars. In relation to the stress, the samples can be classified into three distinct groups: (1) the Nos. 3–7 samples set with defects with high oxygen decoration and smaller open volume (higher peak in Fig. 4), (2) the Nos. 1 and 2 samples set along with the *a*-C sample, characterized by a larger but less decorated open volume, and finally (3) the sample No. 8 with intermediate decoration level of defects.

About the origin of the observed defects, it is most likely that the compressive stress produced during the film growth

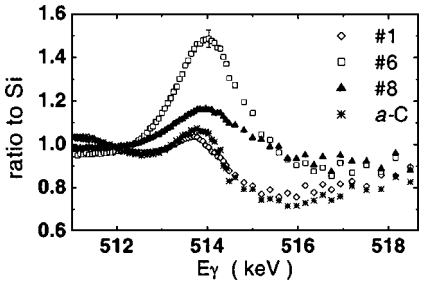

FIG. 4. Characteristic Doppler broadened ratio curves for positron annihilating into defects in the defected Si layer for Nos. 1, 6, 8, and *a*-C samples. The error, associated to the extraction of the characteristic curves from the data, is reported on No. 6.

partly relaxes, creating dislocation movement into the Si substrate instead of directly generating open volume therein. These would explain the deep extension of defects detected by DP–PAS. Vacancies could be formed by jog dragging and also agglomerate to form stabilized clusters. Vacancies and vacancy clusters, bounded to dislocations, act as strong traps for positrons,[19] and can also become attractive sinks for oxygen, giving rise to the observed complexes.[17] The decoration process seems to pursue in time (Fig. 3) with very low activation energy, so a further stress relaxation cannot be excluded. Indeed, in the freshly deposited materials the lower stress is associated with more defects decoration.

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