Investigation of Micropores in Amorphous Hydrogenated Carbon by a Pulsed Positron Beam

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The positron lifetime (PLT) in a thin film of amorphous hydrogenated carbon (a-C:H) was studied by a pulsed positron beam. For the first time the PLT was measured in a layer which is as thin as 100 nm. PLT's of 400(5) ps for the surface state and 348(3) ps in the volume of the film were obtained. The diffusion length of the positrons was measured to be only 4(1) nm. From these results we conclude that in the specimen investigated at least 3% of the total volume is occupied by micropores about 0.5 nm in diameter which may make possible the diffusion of molecular hydrogen in a-C:H.

Recently, a-C:H films have gained considerable interest. They incorporate a large fraction of sp^3-coordinated carbon atoms and hence exhibit diamondlike properties.[1] In controlled nuclear fusion devices the *in situ* coating of all surfaces facing the plasma with typically 50 nm of a-C:H (carbonization) leads to a strong decrease of plasma impurities and to a significantly improved plasma performance.[2] The carbonization technique was first developed for the tokamak TEXTOR.[2] It is now successfully used in various fusion devices.[2-4]

When prepared at a temperature $< 170\,°C$, a saturation concentration of hydrogen H/C$=0.4$ is measured in a-C:H.[5] Upon heating, hydrogen molecules are released in a very broad temperature range up to $1200\,°C$.[5] The repeated interchange of hydrogen between the plasma and the wall (hydrogen recycling) in a tokamak depends on the wall temperature and on the plasma flux to the wall, as well as on the duty cycle of the tokamak pulse operation.[6,7] The recycling processes determine the evolution of the plasma density during a tokamak discharge. Experiments indicate that the recombination of hydrogen atoms into molecules occurs in the bulk of a-C:H.[7,8] Moreover, the permeation of hydrogen through a thin iron membrane coated with a-C:H clearly shows that a rapid transport of molecular hydrogen occurs whereas protons are immobile.[5,9] The paths along which these molecules migrate are still unclear.

Unlike graphite, which has macroscopic grains and pores, a-C:H layers have been shown to be completely amorphous.[5] Transmission electron microscopy measurements exhibit diffuse diffraction patterns. They further reveal a granular structure on the scale of 1-2 nm which cannot be further resolved by the transmission electron microscope.[5,10] It has been speculated that connected micropores of submicroscopic dimensions may be responsible for the rapid molecule transport in a-C:H. From the well-known molecular transport of hydrogen in intercalated graphite $C_{24}K$,[11] a minimal dimension of only 0.2×0.3 nm^2 for these micropores is required.

Positron annihilation is a standard method for the study of submicroscopic pores. Details may be found in a recent review[12] and in the proceedings of recent conferences.[13,14] In many materials a clear relationship between the positron lifetime (PLT) and the size of micropores has been established.[15]

Furthermore, the PLT's for various positron states in diamond and graphite are known[16-18] and collected in Table I. Up to now PLT measurements in a-C:H layers have been prohibited by the fact that the penetration depth of positrons from typical β^+ sources (200 μm in carbon) exceeds by orders of magnitude the thickness of the a-C:H films. Even in the related case of amorphous silicon, where layers up to 70 μm are available, the PLT measurements are difficult[19] and the results are controversial.[20] For a-C:H layers of only 100 nm, slow posi-

TABLE I. PLT data for carbon.

Specimen	Positron state	Lifetime (ps)
Diamond[a]	Bulk	115(1)
Diamond[a]	Surface	365(20)
Graphite[b]	Bulk	210(5)
Graphite[c]	Vacancy	245(5)
Graphite[c]	Large defect	300–400
Graphite[b]	Surface	397(3)
SiC[a]	Surface	423(20)

[a]Reference 16.   [c]Reference 18.
[b]Reference 17.

trons of a few kiloelectronvolts energy have to be used. Although continuous positron beams in this energy range are available now at many places, for the PLT measurements a pulsed positron beam is required.[21] Such a device with a pulse length of about 180 ps has been completed only recently.[22]

The present investigations have been performed with a total time resolution of 240 ps (FWHM). For each beam energy E_{pos} a time spectrum of about 1.8×10^6 events was collected within 8 h. From the total spectrum a time interval of about 4 ns was analyzed with a modified version of the POSITRONFIT routine.[23] The variances of the final fits were 1.1 or less.

The sample preparation by a radio-frequency–assisted dc glow discharge on a single crystal of silicon is described in Ref. 5. From the deposition conditions of the film, the thickness of about 100 nm, the density of about 1.4 g cm^{-3}, and a H/C ratio of 0.4 are known.[5]

In Fig. 1 the results of PLT measurements are shown as functions of the beam energy E_{pos}. The estimated mean penetration depth $\bar{x}$ of the implanted positrons is given in Fig. 1 as well. The calculation of $\bar{x}$ will be considered in a subsequent section. Up to positron energies of 2.5 keV, only a single PLT τ_2 can be observed which for all beam energies remains in the range between 355 and 425 ps which is characteristic for the annihilation at surfaces or at large defects (cf. Table I). Therefore all positrons annihilate from either surface or defect states. Probably τ_2 is the centroid of a distribution of defect lifetimes. However, by numerical checks the total width of this distribution has been proven to be less than 100 ps. For beam energies above 3 keV a second lifetime τ_1 appears whose intensity I_1 increases rapidly with increasing energy E_{pos}. Since $\tau_1 = 220$ ps is the well-known lifetime of positrons in the bulk of silicon,[16] this lifetime is due to the annihilation of positrons which have been implanted into the silicon substrate. The considerably reduced value of τ_1 for beam energies below 4 keV is due to back diffusion of the positrons to the interface between a-C:H and silicon. The short lifetime τ_1 will not be considered further because it is a property of the silicon substrate and it is unimportant for the microstructure of a-C:H. The characteristic shape of τ_2 as a function of E_{pos} will be used to reveal the defect concentration in a-C:H by a model which is sketched in Fig. 2: Positrons which are implanted with the lowest energies annihilate preferentially from the surface state with a lifetime τ_s which is similar to the one reported for graphite (see Table I). At higher beam energies the positrons will diffuse in the bulk of a-C:H or in the silicon substrate until they are trapped either at defects in a-C:H, at the surface, or at the interface between a-C:H and silicon with positron lifetimes τ_d, τ_s, and τ_I, respectively. The diffusion is described by the diffusion lengths L_{Si} and L_a in the silicon substrate and in a-C:H, respectively. Therefore τ_2 is an appropriately weighted average of
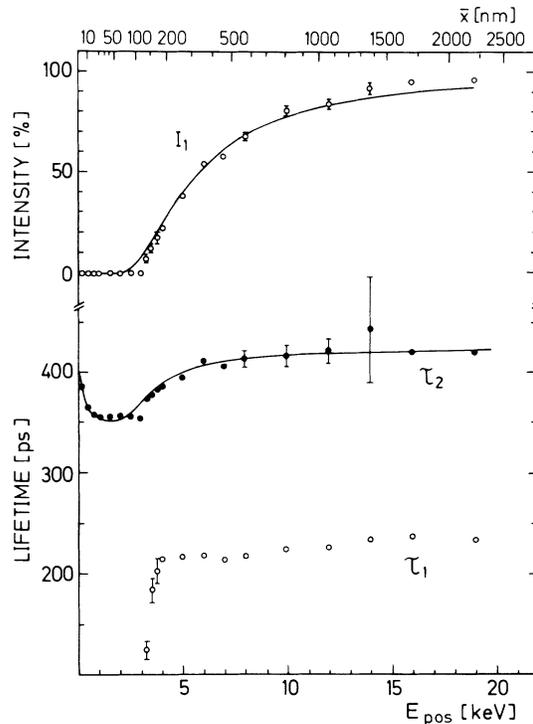
FIG. 1. Results of PLT measurements for a-C:H deposited on a single crystal of silicon. Error bars are given only when exceeding the size of the symbols for data points. Only for 16 and 19 keV the PLT τ_2 was fixed to 425 ps. Solid lines are a result of the fitting procedure described in the text.

τ_s, τ_d, and τ_I. This model has been fitted to the data of Fig. 1. We have used the most probable implantation profile[24] $n(x) = 2x \exp(-x^2/x_0^2)/x_0^2$ with a shape parameter $x_0(E_{pos}) = AE_{pos}^{1.6}$.[24] With the abbreviation $F = \exp(-d^2/x_0^2)$, where d is the thickness of the a-C:H layer, we obtain from this model and from an approximate solution for the diffusion of the positrons the inten-
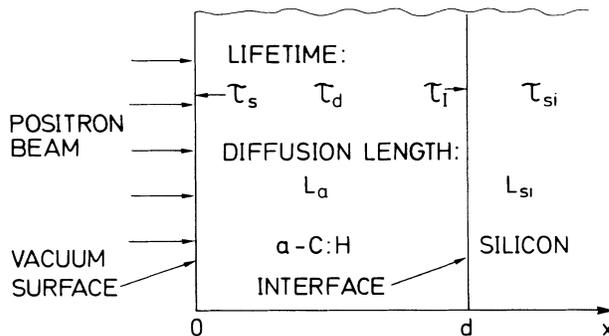
FIG. 2. Notations used in the fit.

sity I_1 and the lifetime τ_2:

$$I_1 = \bar{x}_{Si}(1 - F)/(L_{Si} + \bar{x}_{Si}),$$

$$\tau_2 = \{F(\tau_s L_a + 0.8862\tau_d x_0)/(L_a + 0.8862 x_0) + (1 - F)\tau_l L_{Si}/(L_{Si} + \bar{x}_{Si})\}(L_{Si} + \bar{x}_{Si})/(L_{Si} + F\bar{x}_{Si}).$$

Here $\bar{x}_{Si}$ is the first moment of the positron implantation profile into silicon after passage of the beam through the a-C:H layer. A, τ_s, τ_d, τ_l, d, L_a, L_{Si} are regarded as variable parameters. The best fit obtained is shown in Fig. 1. The fitted values of the parameters are reported in Table II. In spite of the large number of free parameters, quite narrow limits are obtained for their best values because there are always regions in I_1 or τ_2 which are particularly sensitive to a single parameter only. The value of τ_2, for instance, depends mainly on τ_d in the region 1 keV $< E_{pos} <$ 3 keV.

Before discussing the results for the micropores, we will give a few comments on the less important parameters. The fitted value for A is considerably lower than the value $A = 32(3)$ nm which is obtained from the universal relation $A = 45(4)/\rho$ nm, where ρ is the density in grams per cubic centimeter.[24] This relation was derived for materials with higher Z numbers than carbon. Therefore the difference is either due to a wrong value of the density of our a-C:H specimen or to a higher stopping power of a-C:H for positrons as compared with materials with higher Z values. In order to study the influence of Z, a foil of evaporated carbon (97 μg/cm^2) was investigated by the pulsed beam as well. This foil was on a substrate of deformed copper. For beam energies up to 5 keV only a single PLT of 395(3) ps was observed. This indicates a complete positron trapping at grain boundaries (cf. Table I). At higher beam energies a second PLT of 185(5) ps could be resolved which is ascribed to the annihilation of positrons in the substrate. A fit to the intensities as functions of the beam energy resulted in $A = 40(4)/\rho$ nm. If the density of our specimen was evaluated correctly the deviation in A from the universal relation must be due to the hydrogen content of a-C:H. Good agreement with published data is observed for τ_s,[17] L_{Si},[25] and τ_l.[26] The value of τ_l, which is definitely larger than the PLT τ_s at the free surface of the sample, coincides with the surface lifetime in SiC,[16] in agreement with the reported formation of SiC at the boundary of silicon and a-C:H.[26]

The important results for the size and the concentration of the microvoids are the values of τ_d and L_a. τ_d is nearly twice the value for the PLT that we expect for annihilations in the amorphous matrix which is a three-dimensional network of trigonally and tetragonally coordinated carbon atoms.[1] Like positrons in diamond, positrons in the bulk of a-C:H cannot avoid the dense-packed structure, in contrast to the situation in graphite where positrons can avoid the dense-packed hexagonal planes. This fact is clearly demonstrated by a recent angular correlation study.[27] Therefore τ_d is the PLT for annihilations from a defect; the bulk lifetime τ_b for the a-C:H matrix is expected to be even smaller than that of graphite. Unfortunately, besides the data quoted in Table I, we have been unable to find more direct theoretical or experimental evidence for the correlation of PLT and defect size in a-C:H. In the related case of amorphous silicon longer PLT's have been observed,[19,20] but the corresponding defect sizes are controversial.[20] Thus the following discussion is based on the generally accepted picture for metals.[15]

The PLT will increase monotonically from the value τ_{1V} for a single vacancy in graphite to a value of τ_s for an infinitely large defect. The experimentally observed lifetime τ_d can be described by the relation $\tau_d = (2\tau_s + \tau_{1V})/3$ which in the materials Al and Mo is valid for spherical voids containing 8 to 15 vacancies.[15] For a-C:H such a spherical defect would have a diameter of 0.52–0.64 nm. Around this defect size the maximum of the wave function of the trapped positron moves from the center of the defect towards the walls according to Ref. 15. This transition in the shape of the wave function was used to estimate the width of a planar gap necessary for a lifetime τ_d on the basis of published results for positron surface states.[28,29] On the basis of these calculations, the gap width for all metals is in the range 0.28–0.50 nm,[28] or about 1 nm.[29] Obviously the diameter of a tubular defect with a PLT of τ_d should be between the estimated value for a spherical and for a planar defect. In any case, τ_d indicates a defect size that clearly exceeds the minimum cross section of 0.2×0.3 nm^2 required for the diffusion of molecular hydrogen according to the studies on hydrogen charging of intercalated potassium $C_{24}K$.[11] The probable decoration with hydrogen and the expected irregular shape of the defects in a-C:H have been neglected in the discussion above because both would have the tendency to increase the defect size required for a given PLT. Moreover, a distribution of defect sizes, reflected in a distribution of defect lifetimes from about 250 to 400 ps, is expected for an amorphous material. The observed narrow distribution indicates either the less probable formation of a unique defect size or the more probable situation of a system of connected defects of various sizes, where the positrons may diffuse from the primary trapping sites to larger defects with larger bind-

TABLE II. Results for the fitted parameters.

τ_s (ps)	τ_d (ps)	τ_l (ps)	A (nm)	d (nm)	L_a (nm)	L_{Si} (nm)
400(5)	348(3)	425(5)	23(2)	120(10)	4(1)	115(10)

ing energies of the positrons. In the latter case, L_a will exceed the true diffusion length of the positrons in the amorphous matrix. Any inhomogeneity close to the surface will result in a further enhancement of L_a. Therefore the defect concentration will be underestimated if derived from L_a. Denoting by L_0 the diffusion length of positrons in a defect-free a-C:H matrix and by K the specific trapping rate of vacancies in this matrix, we obtain for the concentration of the vacancies c_v clustered into the micropores $c_v = L_0^2/L_a^2 \tau_b K$.[30] L_0 is expected to resemble the diffusion length in crystalline carbon as well because the diffusion of positrons is phonon limited.[15] For diamond a diffusion length $L_0 = 100$–300 nm is reported,[15] whereas a value of $L_0 = 103$ nm for the diffusion parallel to the c axis in graphite has been observed.[31] Since the diffusion perpendicular to the c axis of graphite should be even faster, we use $L_0 = 100$ nm as a lower limit for a-C:H. The trapping rate K is dominated by the available phase space for the creation of electron-hole pairs to absorb the binding energy of the positrons.[15] Because a-C:H is an insulator with a band gap of about 1.5 eV,[11] K should be considerably smaller than the typically 10^{14} s^{-1} observed for metals.[15] With $\tau_b = 200$ ps and $K = 10^{13}$–10^{14} s^{-1}, we find $0.03 < c_v < 0.3$. The upper limit for c_v agrees with the simple model that a-C:H contains micropores in an amorphous matrix—however, with the density of graphite. In any case the size as well as the density of the micropores in a-C:H appear large enough to assist the diffusion of molecular hydrogen.

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