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Positron-annihilation study of voids in a-Si and a-Si:H

Y. J. He,* M. Hasegawa,† R. Lee, and S. Berko
Physics Department, Brandeis University, Waltham, Massachusetts 02254

David Adler and Ai-Lien Jung‡
Center for Materials Science and Engineering, Massachusets Institute of Technology, Cambridge, Massachusetts 02139

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Angular correlation of positron-electron annihilation radiation (ACAR) experiments and positron-lifetime measurements have been performed in a-Si and a-Si:H films as a function of temperature. Positronium formation in microvoids is observed in a-Si:H, but not in a-Si. From the width of the narrow positronium ACAR components we estimate the average diameter of the microvoids to be ≈ 20 Å. A complex temperature dependence of the positron and positronium lifetimes is obtained and is discussed in terms of temperature-dependent positron trapping in various sites and in terms of hydrogen detrapping from dangling bonds.

I. INTRODUCTION

During the last decade amorphous silicon (a-Si) and hydrogenated amorphous silicon (a-Si:H) have been the focal point of many diverse studies[1] designed to elucidate their electronic behavior and their microstructure. The main effect of hydrogenation is the reduction of dangling-bond density by as much as three orders of magnitude, as observed by ESR experiments.[2] The presence of small voids has been well established in both materials by small-angle neutron scattering.[3] More recently, calorimetric[4] as well as infrared[5] experiments indicated the presence of high-pressure molecular hydrogen located in these microvoids.

Positron (e^+)- annihilation experiments have been successfully used to study electronic structure as well as defect properties.[6] In particular, thermalized positrons are known to be captured in radiation-produced voids in metals.[6] It is thus natural to apply e^+ techniques to the study of defects, particularly of voids, in a-Si and a-Si:H. Positron lifetimes depend on the electronic density at the site of the positron and can be used to characterize the nature of the e^+ trapping site in defected materials, including crystalline semiconductors.[7] The angular correlation of annihilation radiation (ACAR) technique,[8] on the other hand, provides a detailed measure of the momentum density of the electrons sampled by the positron. To date only a few e^+ studies have been performed on amorphous silicon systems: Lifetime measurements as a function of annealing temperature were reported in a-Si and a-Si:F,[9] and lifetime-temperature measurements in a-Si and a-Si:H were recently published over a limited temperature range[10] (-130 to $20\,^\circ$C); a momentum measurement using Doppler broadening was also made[11] in a-Si and a-Si:H at room temperature. In this paper we report the first ACAR measurements as well as detailed temperature-dependent lifetime results obtained on samples of a-Si and a-Si:H. Positronium (Ps), the bound e^+-e^- atom,[12] is observed in a-Si:H, but not in a-Si, and the characteristic narrow Ps ACAR component is used to estimate the average microvoid size. Effects due to hydrogen effusion are also described.

II. EXPERIMENTAL

Both a-Si and a-Si:H films were rf sputtered on n-type (10–20 Ω cm) single-crystal (c-Si) wafers in an argon or argon + 12 at.% H_2 atmosphere with the wafers kept at 280° C. The pressure before and during sputtering was 1.2×10^{-7} Torr and ~ 0.015 Torr, respectively. The thickness of the a-Si sample was ~ 100 μm and that of the a-Si:H sample ~ 90 μm. These unusually thick films were required to assure a substantial positron annihilation in the films. Both a-Si and a-Si:H films showed columnar structure by optical microscopy with the column axis perpendicular to the film surfaces. From weighing we estimate a density reduction of $\sim 9\%$ for the a-Si and $\sim 17\%$ for the a-Si:H films from the c-Si value. We estimate that for the a-Si:H sample $\sim 57\%$ of all positrons (from a ^{22}Na source) annihilate in the amorphous film, while $\sim 43\%$ annihilate in the c-Si substrate. The corresponding estimated values for the a-Si sample are ~ 61 and $\sim 39\%$, respectively.

Positron spectra were obtained with a standard lifetime system having a full width at half maximum (FWHM) time resolution of 270 ps. The ACAR data were obtained with the Brandeis multidetector two-dimensional (2D) ACAR system.[13] Multiple slits corresponding to a 2D FWHM of 0.65 mrad were used. During the lifetime as well as the 2D ACAR measurements, the samples were mounted in variable temperature Dewars under a $\sim 10^{-6}$ Torr vacuum.

III. RESULTS

Two-dimensional ACAR measures the 2D projections $N^{2\gamma}(p_y,p_z)$ of the 3D momentum density $\rho(\mathbf{p})$: $N^{2\gamma}(p_y,p_z) = \int \rho(\mathbf{p})dp_x$. For the sake of simplicity we show only the $p_y=0$ cuts of the 2D $N^{2\gamma}(p_y,p_z)$ in Fig. 1. From the measured anisotropic $N^{2\gamma}(p_y,p_z)$ of the c-Si oriented crystal substrate, we can estimate the total amount of annihilation in the substrate contributing to the data of Fig. 1. We find that $\sim 54\%$ of all positrons annihilate in the a-Si and a-

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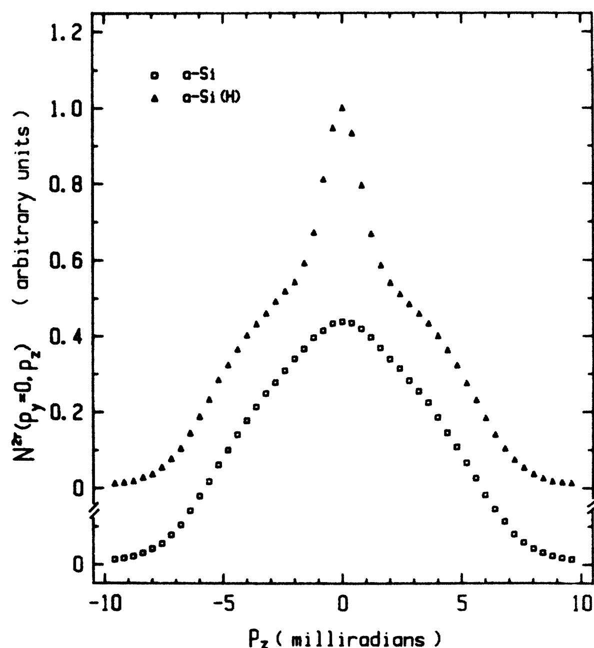

FIG. 1. Cross section through the 2D ACAR data $N^{2\gamma}(p_y,p_z)$ at $p_y=0$, for a-Si and a-Si(H). In momentum units, 1 mrad $\equiv 10^{-3}$ mc.

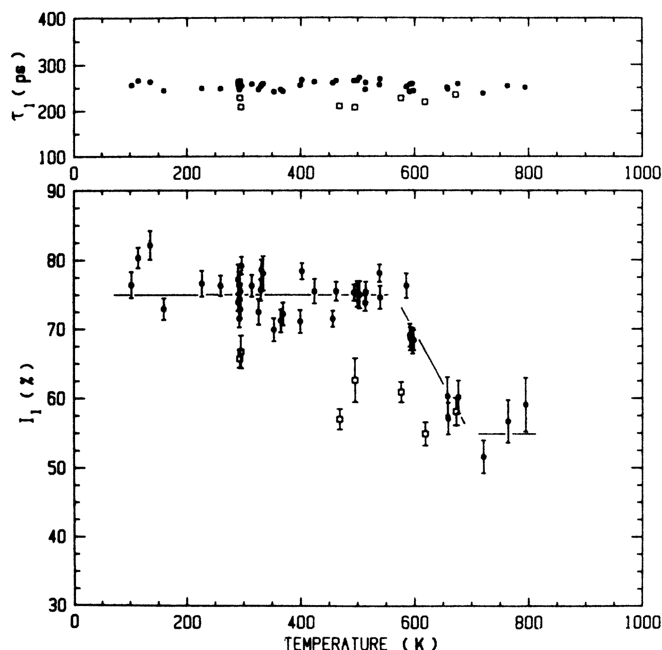

FIG. 2. Lifetime τ_1 and the corresponding intensity vs temperature. Solid circles for a-Si(H) and squares for a-Si. The lines drawn through the a-Si(H) data are linear segments to guide the eye.

Si:H films, in reasonable agreement with the estimates from e^+ range computations, given the difference in geometries. A narrow, nearly Gaussian component of ~ 1.8-mrad FWHM (1 mrad$\equiv 10^{-3}$-mc momentum units) is present in the a-Si:H, but not in the a-Si data. Experiments were performed at several temperatures between 100 and 500 K, without indicating a noticeable change in the shapes of the narrow $N^{2\gamma}(p_y,p_z)$ component.

The lifetime spectra were measured at many temperatures from 100 to 800 K; each spectrum contains at least 1.5×10^6 counts. The spectra were analyzed by an unrestricted POSFIT program[6] into three lifetimes. We plot in Figs. 2–4 the three lifetimes and their corresponding intensities as a function of temperature. We obtain a nearly temperature-independent average τ_1 of 256 ± 1 ps for a-Si:H and of 220 ± 2 ps for a-Si. For a-Si:H, the intensity I_1 remains nearly constant at 75% in the temperature range of 100–550 K and decreases to $\sim 55\%$ at ~ 800 K. A more gradual decrease from ~ 67 to $\sim 57\%$ is observed in the a-Si sample. A nearly constant τ_2 averaging 547 ± 3 ps and 476 ± 4 ps is observed in the a-Si:H and the a-Si, respectively. The corresponding intensities I_2 change oppositely to I_1, since $I_1+I_2\sim 1$ to within a few percent. The large fluctuations in I_1 and I_2 are due to the fact that, in order to observe the longest component τ_3, the lifetime setup was set to sample 95 ps per channel; a small shift in the centroid of the curves during data taking results in a large shift in the effective I_1 and I_2 values. Finally, a surprisingly long third lifetime is found averaging ~ 9 nsec below ~ 450 K; τ_3 decreases to ~ 2 nsec at ~ 650 K and above. The intensity I_3 undergoes an increase from ~ 2 to $\sim 3.5\%$ from 100 to ~ 450 K followed by a decrease above the temperature to $\sim 0.2\%$ at 800 K. From the shape of the raw lifetime data we conclude, however, that τ_3 represents only an average of what appears to be a distribution of long lifetimes. However, due to the low I_3 intensity, present statistics prohibit the analysis of the data in this time region into more than one (average) component.

Attention is to be drawn to the fact that all intensities in Figs. 2–4 are "as measured," i.e., they include an $I_c \simeq 43\%$ (39%) annihilation in the c-Si substrate. The c-Si sample contributes a single lifetime of ~ 220 ps (Ref. 7). The τ_1

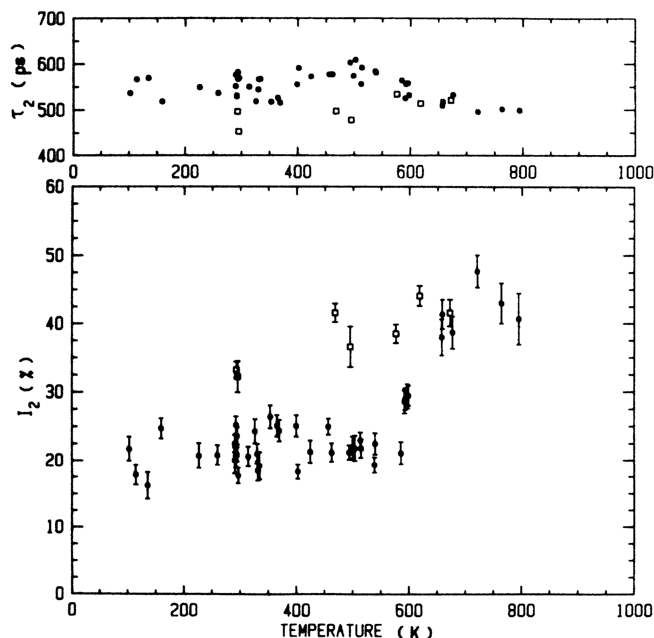

FIG. 3. τ_2 lifetime and the corresponding intensity vs temperature. Solid circles for a-Si(H) and open squares for a-Si.

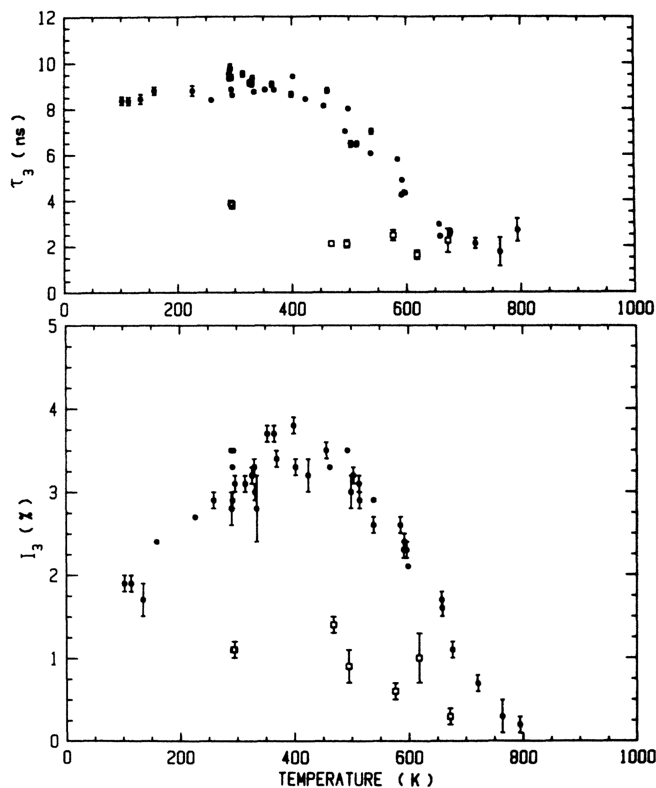

FIG. 4. τ_3 lifetime and the corresponding intensity vs temperature. Solid circles for a-Si(H) and open squares for a-Si.

component corresponds to an average between the 220 ps c-Si τ_1 and the τ_1^a of the amorphous flim. The I^a intensities corresponding to annihilation in the amorphous films alone can be obtained by the simple rescaling of I. We have $I_1^a = (I_1 - I_c)/(1 - I_c)$ and $I_{2,3}^a = I_{2,3}/(1 - I_c)$.

The lifetime data were taken as a function of increasing temperature; as soon as a change in any of the components was found (i.e., above 450 K), lower-temperature lifetimes were remeasured to check for irreversibility due to annealing or other effects. Except for the last three points at the highest temperatures measured (i.e., above 700 K), the T dependence of I_1, I_2, and I_3 as well as of the corresponding lifetimes was found to be reversible. After the three highest-temperature data, room-temperature data in a-Si:H were found to be irreversibly changed to values statistically equal to those in the a-Si sample.

IV. DISCUSSION

In this paper we shall describe only briefly the possible effects responsible for the complex behavior of the lifetime spectra. The narrow ACAR component and the long lifetime τ_3 clearly indicate positronium (Ps) formation. Since no Ps formation has been observed in dense semiconductors, we postulate that the Ps is formed in voids. The narrow ACAR component measures the momentum distribution of the center-of-mass motion of Ps; we can estimate from the ~ 1.8-mrad FWHM of this component the effective size of the microvoid containing the Ps atom.[14] Assuming a fully Ps reflecting spherical microvoid, we obtain an average void diameter of ~ 20 Å. This value is in reasonable agreement with the estimate one obtains from the ir results.[5] This estimate assumes that the H_2 molecules, if present, do not change appreciably the momentum spectrum of the Ps atom. If, however, H_2 is present at the high pressure corresponding to ≈ 800 amagat, as assumed in Ref. 4, this simple estimate will need perhaps some modification. In H_2 gas (in a large volume), Ps can form a self-consistent bubble prior to annihilation[15] at low temperatures, but not at room temperature or above. How such a picture has to be modified in detail in a small (~ 20 Å) microvoid will need further theoretical study.

The magnitude of τ_3 can be attributed to the ortho-Ps (spin triplet) component annihilating with the electrons of the void surface or with the H_2 electrons by "pick-off" annihilation,[6] contributing to the broad ACAR momentum distribution. If we extrapolate the linear density dependence of the annihilation rate observed for lower densities[15] at 293 K to 800 amagat, we obtain a pick-off lifetime of ~ 7.6 nsec, somewhat shorter than the observed ~ 9 nsec at room temperature. However, measurements of $N^{2\gamma}(p_y,p_z)$ versus magnetic field and magnetic field direction[12] reveal that the Ps responsible for τ_3 and the narrow $N^{2\gamma}(p_y,p_z)$ is spin mixed. We attribute this to a spin-exchange interaction of Ps with the walls of the void—perhaps with dangling bonds. Thus, we attribute the observed τ_3 as only partially due to "pick off" and partially due to spin exchange. This limits the density of H_2 if present, to be below 800 amagat. Details of the magnetic field quenching experiment will be described in a separate paper.

Returning to the two shorter lifetime components, we note that τ_1 and τ_2 hardly change with T, while I_1 and I_2 do. This indicates that I_1 cannot be ascribed to annihilation from a delocalized e^+ bulk state via a simple trapping model,[6] as was done by Dannefaer for a-Si and a-Si:F (τ_1 would have to decrease as I_2 increases above 500 K). Instead, we assume that, due to disorder and the large defect concentration, all the positrons are localized in a very brief time: Those annihilating via the τ_1 component are trapped in what one might call "shallow traps," while another fraction is trapped in microvoids of various sizes and annihilate via the τ_2 component. In radiated c-Si, it was observed that the different magnitude τ_2 components can be attributed to trapping in divacancies and quadrivacancies. Thus, Dannefaer assigns the observed τ_2 of ~ 500 ps in a-Si and a-Si:F to e^+ trapping in rings of five missing Si atoms. (In Ref. 10, the somewhat shorter τ_2 of ~ 400 ps is assigned to trapping the quadrivacancy-type defects in a-Si and a-Si:H.) We like to point out, however, that a lifetime between 400–600 ps can also be characteristic of a surface trapped positron (or perhaps physisorbed Ps).[6] We find it more natural, therefore, to assign at least a part of τ_2 to positrons trapped at the inner surface of microvoids in surface states. Trapping to dangling bonds, particularly in the a-Si sample can also not be ruled out.

The sharp decrease in I_1 (increase in I_2) above 550 K could be attributed to a temperature-dependent positron trapping cross section in the "shallow traps" responsible for τ_1 (i.e., less trapping above 550 K similar to the detrapping observed in amorphous metals,[16]) or to an increased trapping cross section into voids.

The initial increase of I_3 for the a-Si:H sample at temperatures below 450 K can be attributed to a temperature

activated detrapping of the e^+ surface state into Ps entering the microvoid. The temperature at which this occurs is lower than that observed for clean crystal surfaces with slow e^+ experiments;[6,17] the temperature lowering can be due to impurity atoms at the surface, such as Ar and H. The observed decrease of τ_3 from ~9 to ~2 nsec above 450 K, if due to an increase in the spin-exchange rate of Ps with the void walls, can be accounted for by postulating a temperature-reversible detrapping of H from dangling-bond sites at the inner wall of the microvoids. The decrease of I_3 above 450 K can then be due to pinning of the e^+ surface state to a dangling-bond site occupied at lower temperatures by hydrogen. Above 700 K, hydrogen effusion starts, and τ_3 and I_3 revert irreversibly to their values in the *a*-Si sample. In this picture the lack of Ps in *a*-Si is attributable to the pinning of the e^+ surface state to dangling bonds. This preliminary qualitative model involving the trapping and detrapping of Ps and H at the walls of the microvoids will need of course more experimental verification and theoretical, quantitative modeling; at present time it cannot be assumed to be a unique picture required to explain the complex temperature dependence of the e^+ and Ps annihilation data presented in this paper. A small, temperature-reversible increase in the dangling-bond density between 450 and 650 K, if observed by ESR experiments, for example, would be an interesting confirming effect of the above model.

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*Permanent address: Department of Physics, Qinghua University, Beijing, People's Republic of China.

†Permanent address: Oarai Branch, RIISOM, Tohoku University, Oarai, Ibaraki 311-13, Japan.

‡Permanent address: Department of Mathematics and Physics, Beijing Institute of Aeronautics and Astronautics, Beijing, People's Republic of China.

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