Hopping Transport of Positrons in Hydrogenated Amorphous Silicon

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Positron beam timing spectroscopy has been used to investigate positron diffusion in hydrogenated amorphous silicon between 85 and 350 K. The diffusivity is determined from both the contribution of the surface, where the positrons have a different characteristic annihilation rate, and its effect on the shape of the bulk annihilation rate distribution. We observe a single positron state with a temperature independent lifetime of 322 ps. From the temperature dependence of the positron diffusion we show that this is a localized state and present the first ever direct observation of hopping diffusion of positrons in solids. The migration enthalpy for positrons in this state is found to be 17.7(3) meV.

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The fundamentals of positron dynamics in crystalline matter have been well understood for over two decades [1]. In perfect crystals the thermalized positron state is a delocalized Bloch wave. Diffusion occurs by a stochastic random walk, dominated by acoustic phonon scattering, with a mean scattering angle around 90°. In the deformation potential approximation this leads to a $T^{1/2}$ temperature dependence of the thermal positron diffusivity. Over the years this behavior has been confirmed experimentally in a wide variety of materials [2,3]. A stronger temperature dependence may occur when other scattering mechanisms such as polar optical phonons [4] become allowed [5,6]. Strongly localized states occur when the positron is trapped at lattice defects, usually vacancies or vacancy clusters. The binding energies of positrons to these defects are high, typically similar in magnitude to the vacancy formation enthalpy itself, and thus hopping diffusion of positrons is not expected to occur.

In contrast the positron state in amorphous media is not well understood. In part this has been due to the lack of suitable material for fundamental studies. Many amorphous materials used in positron annihilation experiments actually exhibit complex annihilation characteristics indicating the presence of a distribution of open volume defects. In high quality hydrogenated amorphous silicon (a-Si:H) films, which approximate an ideal continuous random network [7], the positrons appear to annihilate from a single state with a lifetime similar to that of the divacancy in crystalline silicon (c-Si) [8,9]. Moreover, positrons in this state appear to be slightly mobile at room temperature [8]. In the Letter we show that this is indeed a localized state, but that contrary to expectation is only weakly localized, and present the first ever direct measurement of hopping diffusion of positrons in a solid.

To study positron diffusion in a-Si:H we performed positron lifetime spectroscopy, on a previously characterized 1 μm thick layer on a Corning 7059 glass substrate [9], using the pulsed low energy positron system in Munich [10]. This system allows a positron lifetime spectrum to be measured at different depths inside the material by measuring the rate of emission of annihilation photons as a function of the time interval between annihilation and the incoming pulse of positrons. The present time resolution of the spectrometer is typically 230 ps at a count rate of 2000 Hz, with a peak to background ratio of 5000:1, measured in a 20 ns time window. The incident energy of the positron beam can be varied continuously up to 20 keV and the temperature of the sample controlled by simultaneous cooling with an evaporation cryostat and heating resistively.

Lifetime spectra, containing approximately 2×10^6 events, were recorded for incident positron energies between 3 and 12 keV, corresponding to mean depths solely within the a-Si:H layer, in 0.5 keV intervals, at temperatures between 85 and 350 K. Examples are shown in Fig. 1 for the two extreme temperatures and incident positron energies of 3 and 10 keV. For 10 keV implantation, there is effectively zero return to the surface at all temperatures, and the spectrum approximates an exponential distribution superimposed on a roughly constant background. The 3 keV distribution differs slightly, but significantly (inset), at all temperatures, from the simple exponential behavior, indicating a return to the surface. This difference is smallest at 85 K and increases monotonically with temperature. There are also indications of spurious peaks in the background due to the annihilation of both backscattered and reemitted positrons. At their present intensity, these do not have a significant influence on the subsequent analysis, described below, which concentrates on changes in the shape of the main part of the spectrum.

The lifetime spectra were modeled assuming a homogeneous material and a perfectly absorbing surface, each with a single characteristic lifetime constant and a single diffusivity [11]. It should be noted that this model makes the implicit assumption that the positron distribution first

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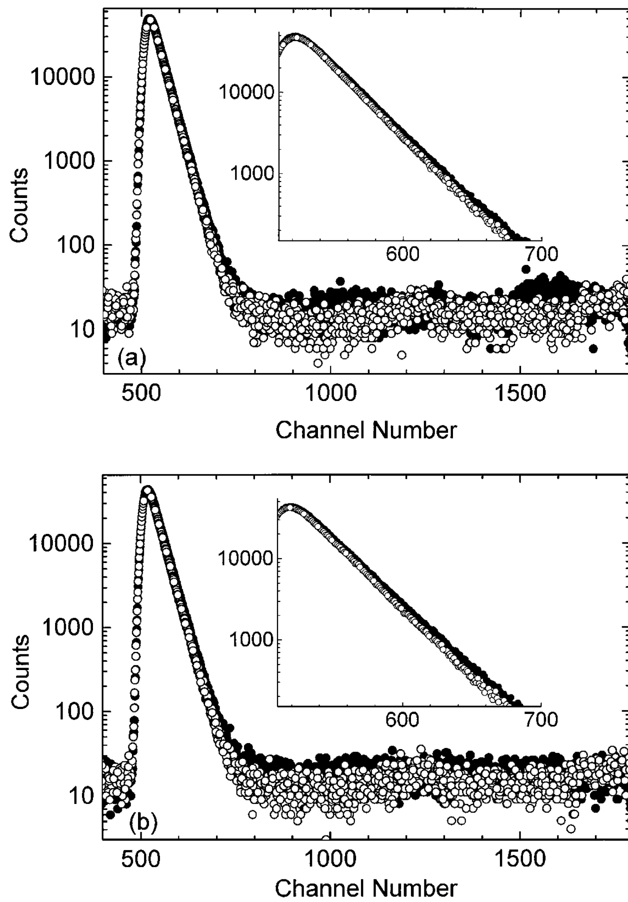

FIG. 1. Positron lifetime spectra measured for 3 keV (●) and 10 keV (○) incident positron energies in hot wire chemical vapor deposition grown a-Si:H at different temperatures: (a) 85 K and (b) 350 K. The inset shows an expanded region at shorter annihilation times.

commences diffusing after being implanted into its initial state with a known depth profile, and that during the diffusion only the spatial extent of the distribution changes.

The resulting lifetime spectrum, before convolution with the instrumental resolution, is given by the weighted superposition of the observed annihilation states, in this case two corresponding to "bulk" and "surface": $N(t) = \lambda_s n_s(t) + \lambda_b n_b(t)$, where the specific annihilation rates λ_b and λ_s are the inverses of the conventional lifetime constants, τ_b and τ_s.

For the commonly used Gaussian derivative form of the generalized Makhovian, $-(d/dz)\{\exp[-(z/z_0)^n]\}$ with $n = 2$, implantation profiles of the time dependent bulk and surface populations, n_b and n_s, are given by [11]

$$n_b = \frac{z_0 e^{-\lambda_b t}}{\sqrt{z_0^2 + 4Dt}},$$

$$\frac{dn_s}{dt} = -\lambda_s n_s(t) + D\,\frac{2n_b(t)}{z_0^2 + 4Dt},$$

where D is the positron diffusivity and z_0 is the range of the initial depth distribution.

The range parameter z_0 was calculated according to widely accepted values as $z_0 = (45\ \mu\mathrm{g\,cm^{-2}\,keV^{-1.6}}/\rho)E^{1.6}$, which have proved to give good agreement with measured layer thicknesses for a-Si:H [8,9]. Noticeable effects of diffusion in the spectra, namely, a dependence on the surface state lifetime and the diffusivity in the shape of the modeled curve, were limited to incident positron energies below 8 keV at room temperature and 5 keV at 85 K. Each spectrum was modeled individually and a consistent set of parameters was extracted for all energies analyzed at a particular temperature. The parameters which were required to be consistent for all spectra recorded at different temperatures were the bulk and surface lifetime constants and the diffusivity. Secondary parameters, such as total area, the time zero, and underlying background, were allowed to vary between beam energies.

The undoped a-Si:H layer was grown by hot-wire chemical vapor deposition and has a band gap of 1.71 eV. In the previous study [9], also using the Munich system but applying conventional positron lifetime analysis, this sample displayed only a single lifetime component in the region of 330 ps, with no evidence of a longer component corresponding to the presence of microvoids. At lower incident positron energies, below 6 keV, the positron lifetime increased slightly, indicating the return of the positrons to a surface state with a characteristic lifetime in the region of 350–360 ps.

Despite the apparent mobility of the positron, this state has a similar characteristic lifetime to the divacancy in c-Si, and is considerably longer lived than the delocalized positron state in c-Si. As the density of a-Si:H is within a few percent identical to c-Si, and the local electronic configurations are also the same, it can be supposed that the lifetime of a free positron in the amorphous network should be similar to that in c-Si. The positron state in a-Si:H should therefore be associated with more open, vacancylike, defected regions of the amorphous network. In terms of the coordination of the atoms in the Si network in a-Si:H, the analog of divacancy is the paired dangling bond defect terminated by one or two hydrogens. This has been interpreted as the dominant annihilation site [9,12], through correlation of the behavior of the positron annihilation characteristics with the behavior of hydrogen on annealing or under illumination. It remains, however, unclear whether this is structurally equivalent to a vacancy-type defect in a crystalline structure, with a significantly larger free volume than other regions in the network. The magnitude of the positron lifetime suggests that this is so, but the positron's slight ability to diffuse suggests otherwise.

In the present experiment we found the diffusivity of the positrons at 300 K to be 0.167(5) $\mathrm{cm^2\,s^{-1}}$, which is about 15 times lower than that found in c-Si using a similar analysis [13]. More importantly the diffusivity has the opposite temperature dependence to that expected for a random walk, showing a strong reduction with decreasing

temperature, reaching 0.034(8) $cm^2\,s^{-1}$ at 85 K. In contrast the lifetime of the positron state remained constant within one picosecond of 322 ps throughout the temperature and energy ranges. The lifetime of the surface state varied between 345 and 365 ps throughout the temperature range measured, but as the surface was neither previously prepared nor well characterized, no consequence will be attached to this observation.

The reduction in diffusion of the positrons could be interpreted in terms of an increase in trapping to negatively charged defects at low temperatures [14]. Such a mechanism could result in the observed temperature independent lifetime if there are two competing positrons states in the bulk of the material, one delocalized and one trapped, with approximately equal annihilation characteristics. Another possibility would be for the trapping rate to a deep defect, with the observed lifetime, to be so high that annihilation from the delocalized state is no longer observed.

The situation of similar annihilation characteristics in the free and trapped states may arise if the trapped state is a Rydberg state around an ionized acceptor [15,16], and the initial state is a freely diffusing positron. However the negligible concentration of acceptors in the a-Si:H layer renders such a scenario unlikely. Additionally the relatively long observed lifetime suggests a rather strongly localized positron state. In general, however, an increase in trapping to any negative center, whether vacancy or negative ion, will be distinguishable from thermally activated hopping by its temperature dependence.

In the a-Si:H network we expect a high concentration of hydrogen terminated dangling bond defects. If the observed positron state is a corresponding localized defect state, trapping of positrons should be saturated and the lifetime constant, as observed. Any observed diffusion of the positrons should therefore result from a hopping transport between these localized states. In this case we should expect a thermally activated process $D = D_0 \exp(-H/kT)$ with a well-defined migration enthalpy H. Such a mechanism had been proposed 20 years ago [17] to explain the observed temperature dependence [18] of the diffusion of quasipositronium (q-Ps)—a small excitonlike state—in amorphous SiO_2. However, the formation of Ps requires a band gap in excess of the Ps binding energy of 6.8 eV and is therefore excluded in a-Si:H. A similar situation may also arise in heavily doped p-type semiconductors, where hopping could occur between Rydberg states around ionized acceptors [16].

In liquid metals [4] phonon assisted hopping diffusion has been suggested as the cause of an observed near exponential increase in the positron diffusion length in Ga at elevated temperatures [19]. However, to our knowledge hopping transport of bare positrons has never been proposed as a transport mechanism or observed for single positron states in solids. The related phenomenon of thermally activated detrapping from shallow trapped states, particularly Rydberg states around negative ions [15] and charged vacancies [20], has been seen in doped c-Si, with an associated Arrhenius behavior of the detrapping rate. While this is a necessary condition for hopping transport, i.e., an Arrhenius behavior of the diffusivity, it alone is not sufficient. For hopping, the thermally activated process has to dominate the dynamics of the diffusing particle, and hence retrapping must be fast compared to the time taken in reaching a neighboring defect, which in turn must be short compared to the residence time in the localized (hopping) state. This may possibly be the case for a high concentration of negative vacancies, as described in [20], where the vacancy core forms a deep trap with a long lifetime, and detrapping occurs from the Rydberg levels of the defect, at a faster rate than the transition to the deep trapped state.

Figure 2 shows an Arrhenius plot of the positron diffusivity D, on a logarithmic scale, against the absolute temperature T, on a reciprocal scale. In this representation, only a thermally activated process, such as hopping, will show a linear temperature dependence. Any other process, such as a dependence of the trapping rate to a negative center, will have a pronounced curvature. The solid line is a weighted linear least squares fit of $\ln D$ to the inverse temperature. From this fit we find a migration enthalpy H of 17.7 $\pm$ 0.3 meV and a temperature independent prefactor D_0 of 0.330 $\pm$ 0.003 $cm^2\,s^{-1}$. As the reduction in diffusivity in the present experiment is seen in the same temperature range as detrapping from Rydberg levels in doped c-Si, we can expect the migration enthalpy in a-Si:H to have a similar magnitude to the Rydberg state binding energy (15 meV for P-V^- [20]). However, in the absence of theoretical studies of positron states and defect levels in a-Si:H, we cannot necessarily draw the conclusion that the two states are the same. Indeed, as discussed above, we can probably exclude the probability of the vacancylike dangling bond defect being charged.

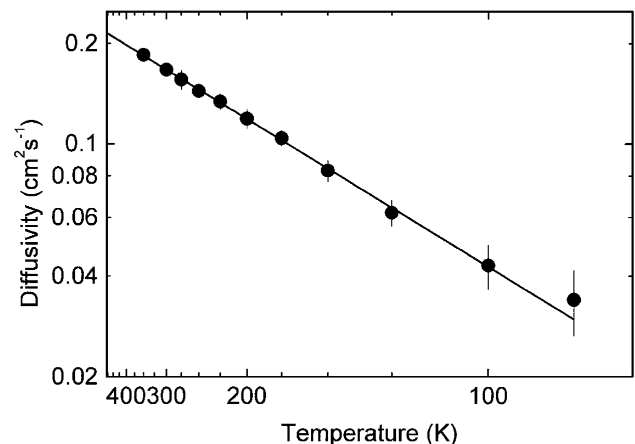

FIG. 2. Arrhenius plot of the positron diffusivity D (logarithmic scale) as a function of measurement temperature T (reciprocal scale) in hydrogenated amorphous silicon. The solid line is a weighted linear fit of $\ln D$ as a function of $1/T$.

We must therefore postulate that hopping arises because of the high density of dangling bond defects and the disordered structure between, leading to only a small energy barrier between neighboring traps, although tunneling between overlapping states through a higher barrier cannot be excluded.

In summary, we have shown that the dominant positron state in a particular covalent random network (a-Si:H) is a localized state, which is probably located at hydrogen terminated dangling bond defects. These are therefore directly equivalent to vacancy complexes in crystalline materials, with an equivalent open volume. In view of this we can further postulate that the slight reduction of density for a-Si:H compared to c-Si is mainly accounted for by the presence of these vacancy-type defects. Unlike in crystalline materials diffusion of the positron occurs via hopping between these localized states. At present the detailed mechanisms of the hopping transport remain unclear, except that the hopping state has a relatively large open volume associated with it, and should therefore, in a crystalline material, have a high binding energy. The most likely cause for the reduction in barrier height is the disorder of the narrow region of the structure between adjacent vacancylike defects, although other mechanisms cannot be excluded.

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