Formation of Hydrogen Impurity States in Silicon and Insulators at Low Implantation Energies

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The formation of hydrogenlike muonium (Mu) has been studied as a function of implantation energy in intrinsic Si, thin films of condensed van der Waals gases (N2, Ne, Ar, Xe), fused and crystalline quartz, and sapphire. By varying the initial energy of positive muons (μ+) between 1 and 30 keV the number of electron-hole pairs generated in the ionization track of the μ+ can be tuned between a few and several thousand. The results show the strong suppression of the formation of those Mu states that depend on the availability of excess electrons. This indicates that the role of H-impurity states in determining electric properties of semiconductors and insulators depends on the way in which atomic H is introduced into the material.

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The implantation of energetic (mega-electron-volt) positive muons (μ+) in insulators or semiconductors commonly leads to the formation of the hydrogenlike bound state muonium [Mu = (μ+e−)] with a final charge state which can be either positive (Mu+), neutral (Mu0), or negative (Mu−). In semiconductors Mu is used to identify and investigate the electronic properties and the behavior of isolated hydrogenlike states [1–3], and hydrogen-related impurities which are of fundamental and technological interest due to their influence on the electrical and optical properties. Isolated H atoms in materials are difficult to detect by other spectroscopic means, which mostly require high H concentrations (see [4,5] and references therein for examples of vibrational spectroscopy studies of Si). In contrast, Mu—which behaves like a light H isotope (mμ = m_e/9)—can be easily detected and characterized by the muon spin rotation (μSR) technique due to its high sensitivity per spin. Muonium states, formed after implantation of energetic μ+, remain isolated during the observational time window of the order of the μ+ lifetime (2.2 μs). Therefore, a large amount of experimental information on the formation, structure and electrical activity of isolated H states in semiconductors has been obtained from μSR, which has played a pioneering role in the identification and characterization of hydrogenlike states. In Si, Ge, and semiconductors of the III-V family two Mu states lying deep in the band gap have been identified at low temperatures (<50 K) [1]: normal MuN, in the tetrahedral interstitial site with a large isotropic hyperfine interaction (HFI) and anomalous MuBC at a bond center between two host atoms with a smaller, anisotropic HFI. In covalent semiconductors, MuN acts as an acceptor and MuBC as a donor. Recently, novel, very weakly bound Mu states (shallow Mu, binding energies 15–60 meV) with very low HFI have been established in a number of II-VI and III-V (nitrides) compounds [6–8]. Theoretical work has shown a universal alignment of hydrogen levels in semiconductors and insulators [9], from which the electronic properties of hydrogen impurities can be derived. The predicted shallow donor hydrogen states in InN and ZnO have been confirmed experimentally by μSR [7,8].

However, it has to be kept in mind that by the techniques used so far the spectroscopically investigated H isotopes are energetically inserted in the solid. This results in a large number Neh of electron-hole pairs generated during slowing down of the incident particle. For instance, all μSR experiments performed up to now used MeV-μ+ beams that generate 105–106 electron-hole pair per implanted μ+ in the ionization track [10]. Similar or higher numbers of excess e− are created by the implantation of H or D ions used in the case of vibrational spectroscopy or channeling experiments. A sizable fraction of these electron-hole pairs escapes prompt recombination and is still present around the thermalized impurity as shown in μSR experiments with applied electric field E of both polarities. The E field clearly changes the Mu formation probability by pushing track e− and μ+ apart or together [11–14], demonstrating that a significant fraction of Mu in semiconductors and insulators is generated by the capture of a track e− after the μ+ has stopped at an interstitial or bond site. In semiconductors it appears that this so-called delayed Mu formation (in contrast to prompt Mu, where Mu forms during slowing down in charge-exchange cycles, followed by thermalization of Mu due to elastic collisions [14]) is the origin of MuBC and for the recently discovered shallow Mu centers in III-V and II-VI semiconductors [12,13,15]. The question therefore arises whether and how the final states are influenced by the formation process, which is essential for studies on technologically important semiconductors and insulators. This can be studied by using the polarized low-energy μ+ (LE-μ+) beam at the Paul Scherrer Institute (PSI, Villigen, Switzerland) [16,17] with variable...
implantation energy between 1 and 30 keV. It allows one to investigate the formation of hydrogenlike Mu impurity states as a function of energy, i.e., as a function of $N_{ch}$. By varying the energy, $N_{ch}$ can be tuned between a few and several thousand. This is up to 5 orders of magnitude less than for conventional MeV-muon beams. Below 1 keV nearly no track products are generated, thus approximating the case where H impurities are thermally introduced, which is how trace atoms are incorporated in the lattice in the course of wafer growth and fabrication processes.

In this Letter we investigate for the first time the formation of thermal Mu as a prototype for isolated H impurities as a function of implantation energy. In addition to intrinsic Si and sapphire ($\text{Al}_2\text{O}_3$) with more than one type of Mu we investigated thin films of van der Waals solids ($s$-Ne, $s$-Ar, $s$-Xe, $s$-N$_2$) and fused and crystalline quartz ($\text{SiO}_2$) due to their simplicity concerning the final charge states: only one type of Mu$^0$ exists with an isotropic HFI close to vacuum Mu$^0$. We find that delayed Mu formation is energy dependent in the keV range in all the investigated samples. Below $\sim 10$ keV the formation of those H-impurity states that require a sizable amount of excess $e^-$ is strongly suppressed. The data on Si and $\text{Al}_2\text{O}_3$ support the interpretations that Mu$_{0\text{BC}}$ in Si [12] and Mu$^+$ in $\text{Al}_2\text{O}_3$ [18] are formed by delayed capture of a track $e^-$. The $\mu$SR technique allows one to differentiate between paramagnetic (Mu$^0$) and $\mu^+$ in diamagnetic environment (free $\mu^+$, Mu$^+$, or Mu$^-$). Because of the hyperfine coupling between the $\mu^+$ and the $e^-$ spin the observable Larmor precession frequency of isotropic Mu$^0$ is about 103 times larger than for the free $\mu^+$. It splits into two intratrillet lines that merge to one line at low fields (<2 mT) where 50% of the muon polarization is not observed due to unresolved hyperfine oscillations between the triplet and singlet state. The diamagnetic and paramagnetic decay asymmetries $A_D$ and $A_{Mu}$ were determined by measuring the amplitudes of the $\mu^+$ and Mu precession signals in transverse (perpendicular to the $\mu^+$ spin) magnetic field, applied parallel to the sample normal. $A_D$ and $A_{Mu}$ are proportional to the fraction of muons in that particular state.

The 0.5 mm thick Si sample with 50 mm diameter (undoped, resistivity 10 kΩ cm, capped by a 2 mm thick oxide layer) was oriented with the (100) direction parallel to the sample normal. The quartz disc samples had thicknesses of 1 and 2 mm [$\text{SiO}_2$ crystal and fused quartz (Suprasil), respectively] and 50 mm diameter. The $\text{Al}_2\text{O}_3$ sample was a 0.5 mm thick single crystal with 60 mm diameter. The solid gas films were grown at partial pressures between $10^{-6}$ and $5 \times 10^{-5}$ hPa. Film thicknesses were about 1000 nm which is sufficient to stop all LE-$\mu^+$ in the layer. At these deposition pressures grain sizes of order 100 nm are obtained [19]. For details on the experimental setup we refer to Ref. [20].

Figure 1 shows typical $\mu$SR asymmetry spectra, and displays the results for Si. In Si, at 5 mT only the precession of the diamagnetic signal is observed. Because of limited statistics and time resolution Mu precession frequencies $>30$ MHz are too high to be resolved with our present setup. In a field of 5 mT, the Mu$^0_{\text{BC}}$ intratrillet lines are at about 70 MHz, whereas the Mu$^0_{\text{BC}}$ transitions are between 35 and 50 MHz, depending on the orientation of the B field with respect to the $(111)$ crystal axis. At 0.5 mT the Mu$^0_{\text{BC}}$ frequencies are nearly unchanged and therefore not observable with our setup, whereas the 7 MHz signal of Mu$^0$ becomes visible. The 0.5 mT data are fitted with two components, a $\mu^+$ precession signal and the Mu$^0$ signal with exponential relaxation, whereas the 5 mT data are fitted with the $\mu^+$ precession signal only. The temperature dependence of $A_D$ at different implantation energies $E_i$ is shown in Fig. 1(a).

![FIG. 1 (color online). (a) Typical $\mu$SR asymmetry spectrum $A(t)$ for the diamagnetic signal in s-Ar, and (b) corresponding signal at low fields showing the 103 times faster Mu precession superposed to the slow diamagnetic signal. (c) Undoped Si, diamagnetic asymmetry $A_D$ as a function of temperature $T$. Solid triangles: implantation energy $E_i > 20$ keV; open squares: $E_i = 9.3$ keV; open circles: $E_i = 2.0$ keV. (d) $A_D$ and Mu$^+_T$ asymmetry $A_{Mu}$ as a function of $E_i$. The lines in (a) and (b) are fits, and in (c) and (d) are guides to the eye.](227401-2)
Mu fraction should be observed; see Fig. 2(b). The different dependence on the availability of excess $e^-$ indicate that the main fraction of $\mathrm{Mu}_{\mathrm{lec}}$ is due to delayed formation, whereas $\mathrm{Mu}_{\mathrm{elec}}^0$ is a consequence of charge-exchange processes at epithermal energies—in agreement with bulk $\mu$SR studies, where an applied $E$ field was used to vary the average distance between $\mu^+$ and excess $e^-$, and therefore the relative formation probability of these two states [12].

Figure 2 shows the energy dependence of $A_D$ and $A_{\mathrm{Mu}}$ for $s$-Ar [2(a)] and SiO$_2$ [2(b)]. Only isotropic Mu is present, and $A_D$ and $A_{\mathrm{Mu}}$ represent a direct measure of the $\mu^+$ and Mu fraction in the sample. The sum $A_{\mathrm{tot}} = A_D + 2A_{\mathrm{Mu}} = 0.263(1)$ is the total observable asymmetry, and there is within the experimental errors no missing fraction. Qualitatively, the $s$-Ar and SiO$_2$ data display the same behavior: with increasing energy $A_D$ is decreasing while $A_{\mathrm{Mu}}$ is increasing correspondingly. The energy-dependent diamagnetic fractions $F_D = A_D/A_{\mathrm{tot}}$ for various insulators are summarized in Fig. 3. With the exception of $s$-Ne all samples show a decreasing diamagnetic fraction with increasing energy. For SiO$_2$ and $s$-Xe bulk Mu fractions $F_{\mathrm{Mu}} = (1 - F_D)$ of 85% and $\sim$100%, respectively, are obtained at 20 keV [corresponding to $\langle d \rangle = 155$ nm (SiO$_2$), $\langle d \rangle = 185$ nm ($s$-Xe)]. At this energy the number of electron-hole pairs created in the ionization track is about 1000 [10]. In the $s$-Ar and $s$-N$_2$ films even at the highest energy the observed Mu fractions ($F_{\mathrm{Mu}} \sim 60\%$) are lower than the bulk results obtained with 4- MeV $\mu^+$ [$F_{\mathrm{Mu}} \sim 100\%$ (s-Ar), $F_{\mathrm{Mu}} \sim 80\%$ (s-N$_2$ at $T < 30$ K)]. The discrepancy is even more drastic for $s$-Ne where the film data are consistent with $F_{\mathrm{Mu}} = 0$ in contrast to the bulk data with $F_{\mathrm{Mu}} = 90\%$ [14]. This disagreement can be explained by the suppression of Mu formation in granular $s$-Ne, $s$-Ar and $s$-N$_2$ thin films, as we discuss below.

The decrease of $F_D$ with increasing $E_i$ reflects the onset of delayed Mu formation with increasing availability of excess $e^-$. From the flattening of $F_D$ at $\sim$20 keV we estimate the number of excess $e^-$ necessary to saturate the delayed Mu yield to be of the order of thousand. The $e^-$ may escape recombination with the $\mu^+$ by several processes: recombination with a cation from the ion track, trapping at grain boundaries, voids, and surfaces or escape from the surface ($e^-$ escape depth $\sim$100 nm in $s$-Ar and $s$-Xe [21], $e^-$ mean free path in Si is $\sim$20 nm at 300 K, increasing to $>100$ nm at lower $T$). An additional obstacle for electron-muon recombination is also the large escape depth of 20–100 nm of epithermal $\mu^+$ in wide band gap insulators such as $s$-N$_2$, $s$-Ar, and $s$-Ne [22]: after leaving the charge-exchange cycles where the last $e^-$ are released the $\mu^+$ may move such a distance away from its ionization track, further losing energy inefficiently by elastic collisions. This large $e^- - \mu^+$ separation and the trapping of $e^-$ combine all together to suppress the delayed Mu formation channel in $s$-Ne, $s$-Ar, and $s$-N$_2$. The total suppression of Mu formation in $s$-Ne is probably a consequence of a $\mu^+$ escape depth larger than the typical grain size, making the formation of a delayed $e^- - \mu^+$ bound state unlikely.

The energy dependence at $T < 100$ K of $A_D$ in sapphire (Fig. 4) shows an interesting anomaly compared to the data.
presented so far. At 100 K $A_D$ decreases with increasing energy and reaches its smallest value of 0.025 at 30 keV. This behavior correlates with the onset of delayed formation of Mu$^+$ as seen in other insulators. The energy dependence of $A_D$ becomes less pronounced on reducing the temperature. At 4 K $A_D$ exhibits a minimum at 10 keV and starts to increase again when further increasing the energy. This may reflect the delayed formation of diamagnetic Mu$^-$, as suggested in a previous E-field $\mu$SR experiment where the disappearance of Mu$^-$ with increasing $T$ is interpreted as thermal ionization of Mu$^-$ with an activation temperature of 130 K [18]. A recent theoretical work shows that H$^-$ could be the stable charge state in Al$_2$O$_3$ [23]. Our data support this idea, and that Mu$^-$ is formed by delayed $e^-$ capture.

In conclusion, the measured energy dependence of Mu formation in intrinsic Si and insulators shows as a general behavior that the formation of delayed Mu states requires the presence of the order of thousand excess $e^-$ in the ionization track. With LE-$\mu^+$ H-impurity states can be studied without the generation of a nonequilibrium electron track. From the implantation energies involved we infer that the length scale of that part of the track that is involved in delayed Mu formation is of the order of 100 nm. At energies $< 3$ keV delayed Mu formation is nearly absent. This indicates that the formation of those H-impurity states which heavily depend on the availability of excess $e^-$ is strongly suppressed in cases where the H isotope is inserted in the solid without the concomitant presence of a sizable number of excess $e^-$. This implies, that the role of H-impurity states in determining electric properties of semiconductors and insulators depends on how atomic H is incorporated into the material. The question of the relative importance of different possible H states and their occurrence as native impurity states in semiconductors and insulators is generally not addressed and we hope that our results will foster new theoretical and experimental studies in this area.

We are extending this kind of experiment to the investigation of shallow Mu states: Preliminary data in ZnO show also a decreasing shallow Mu fraction with decreasing implantation energy, which further supports the general trend found in other materials.

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