Muon Channeling in Semiconductors: Evidence for Pionium Formation

G. Flik, J. N. Bradbury, D. W. Cooke, R. H. Heffner, M. Leon, M. A. Paciotti, and M. E. Schillaci
Los Alamos National Laboratory, Los Alamos, New Mexico 87545

K. Maier and H. Rempp
Max-Planck-Institut für Metallforschung, Institut für Physik, and Institut für Theoretische und Angewandte Physik, Universität Stuttgart, 7000 Stuttgart, West Germany

J. J. Reidy
University of Mississippi, University, Mississippi 38677

C. Boekema
San Jose State University, San Jose, California 95192

and

H. Daniel
Physik Department, Technische Universität München, 8046 Garching, West Germany

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Muon-channeling profiles resulting from the decay of positive pions implanted in high-purity Ge and GaAs single crystals with and without illumination have been measured. The change in profiles with illumination demonstrates that the pion decay site is sensitive to the concentration of excess charge carriers produced by photon absorption. This site change is explained in terms of different electronic states of the pion, i.e., bare π^+ and pionium.

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The behavior of hydrogen, its heavier isotopes (d,t), and the lighter hydrogenlike particles [positive muons (μ^+) and positive pions (π^+)] in semiconductors is of considerable interest. A number of experimental techniques (e.g., ion-beam channeling,[1] muon spin relaxation,[2] infrared and Raman spectroscopy[3]) have been applied to this problem, but as yet no consistent microscopic picture has emerged to describe the observed interaction of hydrogen and its isotopes in semiconductors. Using the new technique of muon channeling from implanted positive pions,[4] we have investigated the behavior of these pions in single crystals of Ge and GaAs of the highest available purity. These experiments were conducted at the Biomedical Channel of the Clinton P. Anderson Meson Physics Facility (LAMPF).

Positive pions, which have $\frac{1}{7}$ the mass of protons and a 26-ns lifetime, were implanted into single-crystalline Ge and GaAs targets where they decayed according to $\pi^+ \rightarrow \mu^+ + \nu_\mu$, yielding muons with 4.12 MeV energy. A small fraction $(\sim 10^{-5})$ of these muons undergo channeling along the $\langle 110 \rangle$ crystallographic direction, giving rise to an angular distribution depending on the π^+ decay site. At a distance of 12.5 m from the sample the muon angular distribution was monitored by a two-dimensional, position-sensitive scintillation detector with a spatial resolution of 1.8 cm (yielding an angular resolution of 0.083°) and an energy resolution of 390 keV. This latter quantity is important for the following reason: With increasing depth of pion implantation into the sample an increasing fraction of initially channeled muons will be *dechanneled*,[5] i.e., they will lose the information defining their point of origin as a result of multiple scattering with electrons and host nuclei. These unwanted dechanneled muons were separated from the channeled ones by energy analysis.

Ge and GaAs single crystals of the highest available quality were oriented such that their $\langle 110 \rangle$ axes pointed toward the center of the detector. In order to produce a large concentration of excess charge carriers without introducing impurities that might act as pion traps (as in a heavily doped sample), we directed the radiation from a high-intensity tungsten lamp onto the sample surface. To take advantage of the time structure of the LAMPF pion beam (pulse repetition period 8.3 ms, pulse length $\leq 750\ \mu s$), the light was chopped so that each light pulse overlapped alternate pion pulses striking the crystal. This technique resulted in a high carrier concentration when the light was on and, because of a rapid surface and bulk recombination, an intrinsic concentration when the light was off. The procedure allowed us (1) to observe the effects of different carrier concentrations at the same sample temperature, (2) to reduce the heat load on the sample, and (3) to minimize the effects of any small shift in crystal orientation or drifts in electronics with time.

Most of the photons produced by the tungsten lamp ($T \simeq 3400$ K) and transmitted through the Lucite light guide have energies exceeding the band gaps for Ge ($E_g = 0.67$ eV) and GaAs ($E_g = 1.43$ eV). Upon illumination, carriers are produced at the surface within a depth $\alpha^{-1} \approx 1$ μm, α being the absorption coefficient, whereupon they rapidly diffuse into the bulk. For typical bulk and surface recombination times[6] this diffusion distance far exceeds the 50-μm depth from which the channeled muons emanate. We conclude that within this depth the carrier concentration resulting from illumination is constant, a typical value being $10^{15 \pm 1}$ cm^{-3} for Ge.[7]

In Fig. 1 we show angular distributions of the relative muon-channeling yields for Ge as a function of the angle ψ measured with respect to the $\langle 110 \rangle$ direction. Data are presented for light-on and light-off conditions at two different temperatures. Variation in the sensitivity of the detector over its surface was removed by division of the channeling data at each point on the detector by "random" data, where the channeling peaks are completely washed out by the scattering of a thin gold foil placed between the sample and the detector. The muon-channeling distributions are expected to be symmetrical about the $\langle 110 \rangle$ direction, and the measured muon distributions are found to be symmetrical within errors. Hence an azimuthal average was made about the $\langle 110 \rangle$ direction, yielding the angular distributions in Fig. 1. The plots represent the ratio of channeled-muon intensity to nonchanneled intensity at each angle ψ within an energy interval at the maximum muon energy.

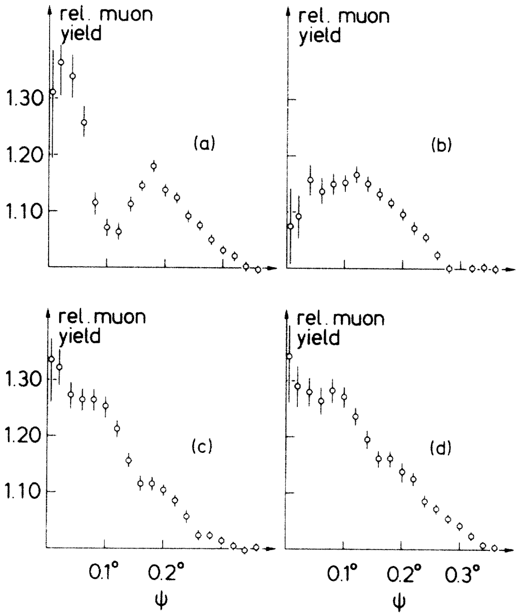

FIG. 1. Angular distributions of relative muon-channeling yields for Ge as a function of the angle ψ measured with respect to the $\langle 110 \rangle$ direction. The data correspond to the following experimental conditions: (a) light off at 100 K, (b) light on at 100 K, (c) light off at 200 K, and (d) light on at 200 K.

At 100 K there are striking differences between the muon angular distributions (channeling profiles) taken with light off and light on [compare Figs. 1(a) and 1(b)]. For example, with light off we see both a central peak (i.e., $\psi = 0°$) and an off-center one ($\psi = 0.2°$), whereas with light on we observe only an off-center peak ($\psi = 0.1°$). At 200 K [see Figs. 1(c) and 1(d)] we observe only slight differences between the light-on and light-off conditions, each profile exhibiting a central peak with hints of possible off-center peaks. We attribute the differences in the muon-channeling profiles observed at 100 K to the occupation of *different pion sites* resulting from an increased carrier concentration during the light-on condition. Furthermore, we note that the pion site (or sites) at 200 K is different from that at 100 K, and is essentially unaffected by light. At 200 K, thermal excitation increases the free-carrier density by $\sim 10^8$ as compared to 100 K, thus making insignificant any increased carrier concentration due to light on.

Figures 2(a) and 2(b) contrast the muon-channeling profiles of GaAs taken at room temperature under light-on and light-off conditions. Qualitatively these results are similar to those of Ge at 100 K [Figs. 1(a) and 1(b)]; i.e., we observe both a central and off-center peak for light off but only an off-center peak for light on. We again conclude that for some temperatures a pion-site change occurs when the free-carrier concentration is increased (light on).

For a qualitative interpretation of the data in terms of specific site occupancy we refer to Fig. 3, which represents the projection of a diamond lattice onto a (110) plane. The position of hexagonal (H) and tetrahedral (T) sites as well as antibonding (AB) sites

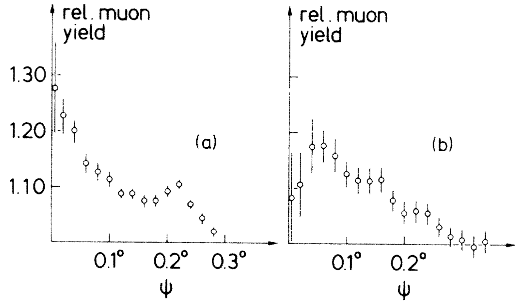

FIG. 2. Angular distributions of relative muon-channeling yields for GaAS as a function of angle ψ measured with respect to the $\langle 110 \rangle$ direction. Data were taken at room temperature for (a) light-off and (b) light-on conditions.

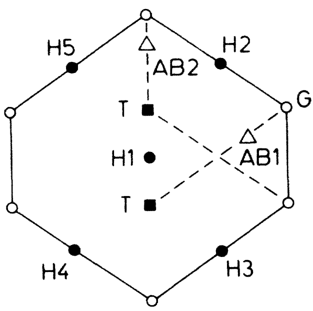

FIG. 3. Projection of a diamond lattice onto the (110) plane. Hexagonal (H1–H5), tetrahedral (T), and antibonding (AB) sites are illustrated.

are shown with respect to the ⟨110⟩ channel. Figures 1 and 2 illustrate muon-flux enhancement, i.e., channeling rather than blocking,[8] so that one can immediately exclude substitutional sites as candidates for possible pion locations. Moreover, channeling theory[8] predicts that pion sites located at or very near a channel center produce muon-channeling peaks centered at $\psi = 0$, whereas off-center sites yield off-center (i.e., $\psi > 0$) peaks. Unfortunately, theoretical efforts have shown that one cannot resolve the T and H1 sites in a muon-channeling experiment. Thus we cannot presently make an unambiguous correlation of observed channeling peaks with specific pion sites. Future work will, however, include muon-channeling profiles taken along ⟨100⟩ and ⟨111⟩ directions as well as (100) planes. Since channeling along (100) planes produces muon-flux enhancement for H sites but diminution (i.e., blocking) for T sites,[5] such data should be useful in differentiating between the two. Nevertheless we discuss the various possibilities for pion sites in Ge and GaAs based upon the present data.

Results for Ge at 100 K and GaAs at room temperature are similar. If H-site occupancy is preferred when the light is off, then the central peak could be due to a pion residing at H1, whereas the off-center peak could be attributed to H2–H5 occupancy. For light on, the pion could preferentially occupy the T site. This interpretation seems plausible on the basis of the angular position of the off-center peak for both Ge and GaAs during light on. That is, we note that the off-center peak occurs at a smaller angle for light on than for light off. One must be somewhat careful with this conclusion, however, since it might be possible to generate the off-center channeling peaks in Figs. 1(b) and 2(b) by appropriate weighting of the central and off-center peaks of Figs. 1(a) and 2(a). This possibility, coupled with our lack of knowledge regarding T- and H-site resolution, suggests a second, equally plausible, interpretation of the observed muon-channeling profiles. The central peaks observed in Figs. 1(a) and 2(a) might be associated with pions occupying H1 and/or T sites, while the off-center peaks represent AB-site occupancy. With light on [Figs. 1(b) and 2(b)], a larger portion of the pions occupy AB sites than H1 and/or T sites, thus yielding an off-center peak. At 200 K Ge exhibits a rather broad central peak for both light on and light off, possibly indicating multiple pion-site occupancy.

Regardless of the uncertainty in specifying pion sites from the observed channeling profiles, it is clear that for certain temperature intervals a pion-site change occurs when the carrier concentration is increased (light on). This effect can be understood qualitatively in terms of different electronic states of the pion. From muon spin relaxation experiments, where positive muons (μ^+) are implanted into semiconductors,[2,9] it is known that muons form different electronic states, viz., diamagnetic (bare) μ^+, "normal" muonium ($\mathrm{Mu} = \mu^+ e^-$) with a spherically symmetric electron distribution, and "anomalous" muonium (Mu^*) with an anisotropic electron distribution, possibly resulting from bond formation. We suggest that normal pionium ($\mathrm{Pi} = \pi^+ e^-$) and anomalous pionium (Pi^*), analogs of the muon states, are formed in Ge and GaAs. We should expect bare-pion (π^+) states as well; however, it seems highly unlikely that a bare pion would occupy different sites as a result of increased charge-carrier concentration.

Hartree-Fock and Hückel calculations[10,11] demonstrate that the lattice potential E_T^* for 1*s* hydrogen isotopes at T sites is an absolute minimum. Thus, formation of Pi should occur at T sites, a location consistent with our data. Furthermore, it is known that the lattice potential E_H^* of 1*s* hydrogen isotopes occupying H sites represents an absolute maximum, with $E_\mathrm{H}^* - E_\mathrm{T}^* = 1.2$ eV for atomic hydrogen in silicon[10] and $E_\mathrm{H}^* - E_\mathrm{T}^* = 0.8$ eV for Mu in diamond.[11] Therefore, low-symmetry H sites should be unstable for Pi. Thus, H-site occupancy is possible only if pionium forms bonds with each nearest-neighbor Ge atom (i.e., Pi^*). Similarly, pionium at an AB site is expected to be chemically bonded with the nearest-neighbor Ge atom with which the AB site is associated. As H and/or AB sites are suggested by our data, we conclude that pionium states exist which cannot be solely explained by formation of Pi at T sites. We associate these states with anomalous pionium (Pi^*).

To summarize, the muon-channeling results presented herein, specifically the observation of a pion-site change, taken together with the theoretical results,[10,11] strongly indicate the existence of both normal pionium and anomalous pionium in Ge and GaAs. To our knowledge, this is the first evidence suggesting the formation of pionium in a solid.

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