



PII: S0038–1098(98)00314-7

SELENIUM DOUBLE DONORS IN NEUTRON TRANSMUTATION DOPED, ISOTOPICALLY CONTROLLED GERMANIUM

C.S. Olsen,^{a,b} J.W. Beeman,^a K.M. Itoh,^{a,b} J. Farmer,^c V.I. Ozhogin^d and E.E. Haller^{a,b,*}^a Lawrence Berkeley National Laboratory^b University of California, Berkeley, CA 94720, U.S.A.^c University of Missouri, Columbia, MO 65211, U.S.A.^d Kurchatov Institute of Atomic Energy, 123182 Moscow, Russia

(Received 18 June 1998; accepted 29 June 1998 by M. Cardona)

Far infrared photoconductivity and absorption measurements were performed on isotopically controlled ⁷⁶Ge samples that were neutron irradiated to produce ⁷⁷Se through double beta decay. The spectra exhibit ground state to bound excited state transitions which place the first ionization level of Se at $E_c-0.2688$ eV. Hall effect measurements on compensated Ge:Se single crystals yield the second ionization level in the lower half of the band gap at $E_v+0.17$ eV. Our experiments offer the first unambiguous identification of the deep donor level formed by single Se atoms on Ge lattice sites and verify earlier findings. © 1998 Elsevier Science Ltd. All rights reserved

Keywords: A. semiconductor, C. impurities in semiconductors.

1. INTRODUCTION

Several attempts have been made to measure the first and second ionization energies of the Se double donor on substitutional lattice sites in germanium. [1–4] Many researchers have identified Se associated energy levels in the bandgap, but also reported that only a small fraction of all chalcogen impurities are electrically active. Tyler introduced Se during crystal growth and observed two Se-related levels at $E_c-0.14$ eV and $E_c-0.28$ eV using Hall effect measurements. [1] Pearton performed Se diffusion and identified slightly different energy positions by Deep Level Transient Spectroscopy (DLTS) at $E_c-0.11$ eV and $E_c-0.30$ eV. [2] Osip'yan attempted to compare the concentrations of $E_c-0.14$ and $E_c-0.28$ eV Se levels reported by Tyler using Neutron Transmutation Doped (NTD) natural Ge, but could not determine the energy levels due to the p-type conversion of the Ge. [3] More recently Grimmeiss diffused Se and performed photoconductivity to identify levels at $E_c-0.268$ eV and $E_c-0.512$ eV. [4] According to these experiments, the second

ionization level lies in the lower half of the bandgap and is always occupied in n-type Ge in equilibrium.

The chalcogens (S, Se, and Te) in Si have been shown to form a large variety of donor complexes involving two or more chalcogen impurity atoms. [5, 6] Therefore special care has to be taken to assure that the observed energy levels in crystals doped with chalcogen impurities are due to isolated double donors on lattice sites and not to multi-atom complexes. The purpose of our experiment reported here is to arrive at an unambiguous identification of the Se substitutional energy levels by applying NTD to isotopically controlled Ge single crystals.

2. SELENIUM DOUBLE DONOR FORMATION THROUGH NTD

NTD has been used for introducing acceptors and donors in a variety of semiconductors at low temperatures. [7] This unique doping process works by irradiating a semiconductor with thermal neutrons. Upon neutron capture, some of the newly formed isotopes are radioactive and decay into doping elements. Be-

* Corresponding author: E-mail: EEHaller@LBL.gov

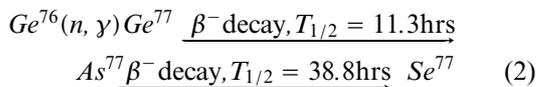
cause the distribution of isotopes in a solid is perfectly random, the neutron source is very large, and the absorption cross sections for thermal neutrons are very small, the doping resulting from NTD is very homogeneous through out the semiconductor sample. The concentration of dopants is given by the following equation:

$$N = A \cdot \rho \cdot n \cdot \sigma_c \cdot t_0 \quad (1)$$

where A is the isotope fraction, ρ is the atom density of the semiconductor (for germanium $\rho = 4.4 \times 10^{22} \text{ cm}^{-3}$), n is the neutron flux ($\text{cm}^{-2}\text{s}^{-1}$), σ_c is the thermal neutron capture cross section (cm^2), and t_0 is the irradiation time (s). The dopant concentration is completely controlled by the neutron fluence ($n \cdot t_0$). The NTD technique is always accompanied by the production of radiation damage due to fast neutrons, fission gamma rays, gamma ray recoil, and beta recoil. This radiation damage must be removed by thermal annealing to observe the dopant levels. The NTD technique is used for doping whole floating zone Si single crystals on a commercial scale for power device applications. [8]

Natural Ge consists of 5 stable isotopes with very well known abundances, as shown in Table 1. Ge is the only semiconductor in which both n- and p-type dopants can be produced by NTD. ^{70}Ge transforms to ^{71}Ga acceptors, and ^{74}Ge transforms to ^{75}As donors. [9]

Upon neutron capture, ^{76}Ge leads to ^{77}Se after 2 β^- decays. Simultaneous emission of two betas and two antineutrinos is possible with a half-life $\sim 10^{23}$ years. [10, 11] The specific advantage of NTD for Se doping is that a single ^{77}Se atom is formed on a substitutional site in the lattice with a very low probability of being dislodged during the β^- decay. The uniform distribution of Se at a low concentration of 10^{15} cm^{-3} ensures that the probability of Se atoms located next to each other is negligible. For natural Ge, the concentration of Se produced will be small compared to the concentrations of Ga and As, due to the low abundance and low capture cross section of ^{76}Ge . Natural ultra-pure Ge is p-type after NTD which makes it difficult to observe the donor levels of selenium. Isotopically controlled Ge is a superior candidate for selenium NTD studies, because the relative Se concentration can be increased arbitrarily compared to the Ga and As concentrations. The decay process for ^{77}Ge is given by:



We will now show how the decay dynamics can be exploited to dope Ge with Se and keep it on Ge lat-

tice sites. In the following discussion, the initial irradiation time (≤ 1 hour) is considered negligibly short compared to the decay times. After thermal neutrons have been captured by ^{76}Ge , ^{77}As begins to form with a half-life of 11.3 hours. The standard definition for the decay constant is $\lambda_A = (\ln 2)/T_{1/2}$. We define the decay constant for ^{77}Ge to be $\lambda_{Ge} = (\ln 2)/11.3 \text{ hrs}$ and for ^{77}As to be $\lambda_{As} = (\ln 2)/38.8 \text{ hrs}$. The concentration of As daughter isotopes produced as a function of time after irradiation is: [12]

$$\begin{aligned} [^{77}\text{As}] &= [^{77}\text{Ge}] \left(\frac{\lambda_{Ge}}{\lambda_{As} - \lambda_{Ge}} \right) \\ &\times (\exp(-t\lambda_{Ge}) - \exp(-t\lambda_{As})) \end{aligned} \quad (3)$$

The ^{77}As formation progresses much faster than the subsequent ^{77}Se formation, because of the large difference in half-lives.

$$\begin{aligned} [^{77}\text{Se}] &= [^{77}\text{Ge}] \left(1 - \exp(-t\lambda_{Ge}) \right. \\ &\left. - \left(\frac{\lambda_{Ge}}{\lambda_{As} - \lambda_{Ge}} \right) (\exp(-t\lambda_{Ge}) - \exp(-t\lambda_{As})) \right) \end{aligned} \quad (4)$$

This difference in the ^{77}As and ^{77}Se formation rates can be selectively exploited in the radiation damage annealing process following the NTD process. For example five hours after the neutron irradiation, only 1.2% of the Se have formed. The remaining 98.8% ^{77}As atoms will assume Ge host lattice positions during the annealing process. Thermal annealing within the first 5 hours, therefore, can lead to thermal displacement of a maximum of 1.2% of all the Se produced. This choice of thermal annealing timing is critical because of the unstable nature of Se on substitutional sites in the Ge lattice. We found from preliminary DLTS studies that Se begins to “deactivate” around 400°C and is less stable than the neutron irradiation damage. This experimental observation dictates that the thermal annealing has to be performed *before* the ^{77}Se is formed. The pre-Se formation annealing process places the intermediate ^{77}As atoms on host lattice sites and most of the ^{77}Se atoms forming over time at room temperature will also occupy host lattice positions. A very small fraction will be displaced from host lattice sites through β^- recoils. Isotopically enriched ^{76}Ge samples (85% ^{76}Ge , 15% ^{74}Ge) were neutron irradiated with a dose of $5.6 \times 10^{17} \text{ cm}^{-2}$, which produces a Se concentration of $3.3 \times 10^{15} \text{ cm}^{-3}$. ^{76}Ge samples were annealed within 2 hours of neutron irradiation to remove the irradiation damage and to return the ^{77}Ge and ^{77}As atoms to their substitutional sites before the final decay to ^{77}Se proceeded. We estimate that 96% of all the

Table 1. NTD parameters of natural Ge [9]

| Isotopes | Abundance (%) | σ_c ($\times 10^{-24}$ cm ²) | Product | $T_{1/2}$ | Type |
|------------------|---------------|--|------------------|----------------|------|
| ⁷⁰ Ge | 20.5 | 3.25 | ⁷¹ Ga | 11.2 d | p |
| ⁷² Ge | 27.4 | 1.0 | ⁷³ Ge | stable | |
| ⁷³ Ge | 7.8 | 15.0 | ⁷⁴ Ge | stable | |
| ⁷⁴ Ge | 36.5 | 0.52 | ⁷⁵ As | 82.2 m | n |
| ⁷⁶ Ge | 7.8 | 0.16 | ⁷⁷ Se | 11.3, 38.8 hrs | n |

Se created by NTD will form isolated substitutional double donors.

3. FIRST IONIZATION LEVEL OF SELENIUM (SE^{0/+})

Photothermal Ionization Spectroscopy (PTIS) and IR absorption spectroscopy were performed on the enriched, NTD doped ⁷⁶Ge. Hall effect measurements do not yield accurate data due to their insensitivity to deep energy levels in the presence of shallow dopants with comparable concentrations. Absorption measurements were accomplished on a Bomem DA8 FT spectrometer in a variable temperature cryostat. Photoconductivity measurements were carried out on a Digilab FTS-20E spectrometer. Contacts were fabricated by implanting P⁺ ions at 40 keV and 100 keV with doses of 2×10^{14} and 4×10^{14} cm⁻², respectively. The sample was maintained at -167°C during implantation which allows for P donor activation to occur at an annealing temperature as low as 330°C. An absorption spectrum of Se^{0/+} in NTD doped ⁷⁶Ge is shown in Fig. 1. A series of hydrogenic ground state to bound excited state transitions were observed for this impurity. By adding 1.73 meV, the Effective Mass Theory (EMT) binding energy of the 2p_± state, [13] to the 1s-2p_± transition energy, a ground state binding energy of 268.85 ± 0.06 meV is found. PTIS measurements showed the same bound excited state transitions as the absorption measurement. The energy spacing between the bound excited state and the conduction band edge are in good agreement with EMT. [14] The bound excited state transition energies are compared to EMT values and values reported for P in Ge in Table 2. A Fano-resonance of a transition from the 1s(T₂) state with a zone center optical phonon of 37.7 meV is also visible in the conduction band continuum. We were also able to detect the 1s(A₁) to 4p_± level transition. This IR spectrum agrees with data published by Grimmeiss [4] on Se diffused Ge, except for a systematic shift of 0.63 meV to higher energy in the 1s(A₁) groundstate. This shift was confirmed on two different spectrometers. The arsenic 1s to 2p_± transition line was located in this sample at 12.43 meV, within 0.01 meV of the Reuszer and Fisher results. [15] Scaled to

Table 2. Summary of hydrogenic excited states of Se^{0/+} level

| | EMT | P | Se (Grimmeiss) | Se (This Work) |
|---------------------|------|-------|-----------------|-----------------|
| 4p _± | 0.61 | 0.62 | | 0.65 |
| 3p _± | 1.03 | 1.05 | 1.04 ± 0.03 | 1.07 ± 0.06 |
| 2p _± | 1.73 | 1.73 | 1.73 | 1.73 |
| 3p ₀ | 2.56 | 2.56 | 2.57 | 2.63 |
| 2s(T ₂) | 3.52 | | 3.58 | |
| 2p ₀ | 4.74 | 4.74 | 4.75 | 4.78 |
| 1s(T ₂) | 9.81 | 9.93 | 9.95 | 9.99 |
| 1s(A ₁) | | 12.76 | 268.22 | 268.85 |

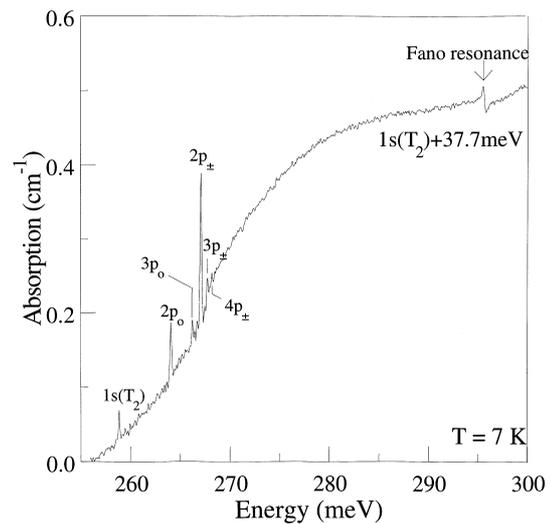


Fig. 1. Infrared absorption spectrum of isotopically enriched ⁷⁶Ge doped with $[Se]=3 \times 10^{15}$ cm⁻³. Several ground to bound excited state lines associated with Se⁰ are visible. A Fano resonance appears at $E(1s(T_2)) + E(LO)$.

the neutral Se binding energy, this error would only account for a 0.22 meV shift.

4. SECOND IONIZATION LEVEL OF SELENIUM (SE^{+ /2+})

An isotopically controlled Ge crystal was grown with 82.8% ⁷⁶Ge, 12.9% ⁷⁴Ge and 4.3% ⁷⁰Ge. NTD of this crystal led to the total compensation of the first ionization level of Se, such that the second ionization level Se^{+ /2+} could be observed. We used a neutron dose exposure and an annealing schedule similar to those used for the enriched ⁷⁶Ge crystal. The

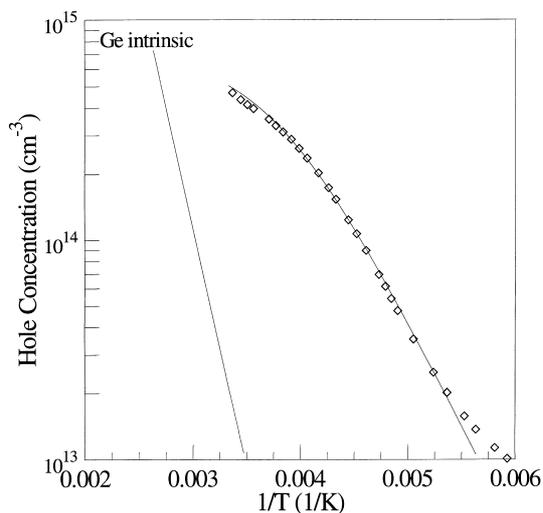


Fig. 2. Variable Temperature Hall Effect of $^{70/74/76}\text{Ge}:\text{Se}$ crystal; a fit to the data points gives $E_{\text{activation}} = E_v + 0.17 \text{ eV}$. For comparison the freeze out curve for intrinsic Ge is shown.

close compensation of the Ge crystal makes variable temperature Hall effect measurements advantageous. Figure 2 shows the freezing out of holes onto the Se^+ state thus ionizing it to Se^{2+} . The activation energy of $E_v + 0.17 \text{ eV}$ observed is in good agreement with the $E_c - 0.512 \text{ eV}$ ionization energy measured by Grimmeiss. [4] Shallower impurities start to dominate the freeze-out at lower temperatures. Absorption and photoconductivity measurements were performed, but due to the low position of the Fermi level at 7 K (overcompensation by acceptors), the second ionization level of Se was depopulated and could not be observed. In agreement with Grimmeiss' result [4], we also find the second ionization level of Se in the lower half of the band gap.

5. CONCLUSION

In summary, our low temperature NTD doping method has resolved the controversy over the true identity of the donor species leading to the first and second ionization levels observed in Se doped Ge. The first ionization stage was identified spectroscopically and the second ionization level was observed in the lower half of the band gap by variable temperature Hall effect. Using proper timing for annealing after NTD we have been able to produce Se double donors which occupy host lattice sites with a large probability.

Further, we can exclude Se-Se pair formation because our crystals are not heated after Se has formed.

Acknowledgements—This work was supported in part by National Aeronautics and Space Administration under contracts W17605 and A59513C through inter-agency agreement with U.S. Department of Energy under contract DE-AC03-76SF00098.

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