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TWO NOVEL ACCEPTORS IN ULTRA-PURE GERMANIUM: NATURE AND INTERCONVERSION

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Experimental data on two shallow acceptors A_4 and $A_{3,5}$ in pure germanium are presented. The two acceptors appear with concentrations up to $\sim 10^{11} \text{ cm}^{-3}$ always and only in ultra-pure germanium single crystals which have been grown in a pure N_2 ambient from a melt contained in a graphite crucible. The bound excited state spectra of both acceptors are hydrogenic. The ground state of A_4 is a Γ_8 quadruplet while the $A_{3,5}$ acceptor exhibits a ground state manifold consisting of at least two Kramers doublets, one with Γ_6 and the other with Γ_7 symmetry. The energy splitting between the two doublets is 1.1 meV and it is symmetric in relation to the position of the A_4 ground state. Complete and reversible interconversion can be induced with appropriate thermal annealing. The experimental results suggest that A_4 and $A_{3,5}$ are two forms of one center. Above 700K the A_4 concentration decreases irreversibly following an exponential decay. Interconversion can be observed at any point during the irreversible annealing of the center.

1. INTRODUCTION

A new class of shallow acceptors and donors has emerged over the past few years from experiments with ultra-pure germanium.¹⁻³ The degeneracy and the symmetry of the ground state of several of these new centers is different from the ground state of acceptors and donors which are due to substitutional or interstitial elemental impurities. The bound excited state spectrum on the other hand is perfectly "hydrogenic", i.e., caused by a hydrogen-like Coulomb potential. Extensive experimental studies on a large number of well characterized ultra-pure germanium single crystals have led to a model which quantitatively describes the ground state manifold of the novel centers.⁴⁻⁶ This model is based on a substitutional impurity (e.g. Si, C, O, Cu) which binds a light, interstitial impurity (e.g. H, Li and possibly N). Rapid tunneling of the interstitial impurity between four equivalent interstitial positions modifies the electronic structure of the ground state. In the case of acceptors, the tunneling transforms the usual fourfold degenerate ground state with Γ_8 symmetry into a sixteenfold manifold with one Γ_6 doublet, one Γ_7 doublet and three Γ_8 quadruplets. The two doublets are stress insensitive (Kramers doublets). They are the lowest lying components of the ground state manifold of the acceptors $A(\text{H}, \text{Si})$ and $A(\text{H}, \text{C})$.⁴ It is likely that several of the hitherto unidentified centers which have been labeled alphanumerically (e.g. A_{10} , A_{11} ,² etc.) belong to the same group of new centers. In this paper we are presenting experimental results on two acceptors which lead to three series of ir-lines. The three series have originally been labeled A_3 , A_4 and A_5 .⁷

2. EXPERIMENTAL TECHNIQUES AND RESULTS

2.1 Photothermal Ionization Spectroscopy

Photothermal Ionization Spectroscopy (PTIS),⁸ a two-step ionization process leading to changes in the low temperature conductivity, combines excellent sensitivity with high spectral resolution. PTIS has been very useful in the study of shallow levels in very pure semiconductors, mainly in germanium^{1,9,10} and in silicon¹⁰ single crystals. A brief description of the PTIS technique will be helpful for the understanding of the section which follows. Figure 1 shows the bound electronic ground and excited states of a donor in germanium or silicon. In uncompensated, donor-doped Ge, all donor electrons will occupy the ground state at low temperatures ($< 10\text{K}$). The absorption of a photon of appropriate energy causes the transition of the electron to a p-like excited state. Subsequent absorption of a phonon can lead to ionization of the donor, i.e., a free electron and a positively charged donor ion. The measurement of the electrical conductivity of a semiconductor sample as a function of photon wavenumber (or photon energy) leads to a photoconductivity spectrum consisting of a series of sharp lines, which are due to photothermal ionization processes, and the well-known photoconductivity continuum. The temperature of the sample under investigation determines the phonon spectrum in the crystal which in turn has a strong influence on the intensity of the photothermal excitation lines. The sharp lines vanish with decreasing temperature and grow with increasing temperature to the point where direct thermal ionization from the ground state begins to reduce the number of

neutral centers. The ideal temperature range for PTIS of shallow centers in germanium spans from ~ 5 to ~ 9 K.

Fig. 1. Illustration of the two-step process leading to Photothermal Ionization Spectroscopy (PTIS), also called Photoelectric Spectroscopy⁸.

Contrary to standard absorption spectroscopy, the sensitivity of PTIS does not depend to first order on the number of shallow centers in a given sample because the "dark" conductivity and the change in conductivity due to photothermal ionization processes are both proportional to the net-dopant concentration. Absorption spectroscopy and photothermal ionization spectroscopy are schematically compared in Fig. 2. In PTIS, the sample under investigation plays the role of the absorber and of the detector simultaneously. Only the absorbed photons lead to a signal. In standard absorption spectroscopy, on the other hand, one determines the number of absorbed photons by measuring the reduction in the photon stream which has passed through the sample. Absorption spectroscopy requires samples with net-acceptor or donor concentrations $> 5 \times 10^{12} \text{cm}^{-3}$, two to three orders of magnitude higher than are present in ultra-pure Ge samples. PTIS, on the other hand, has been successfully used on samples containing less than $\sim 10^7$ centers.

Any conductivity technique requires electrical contacts which can freely inject or extract electrical carriers into and from the sample. Such contacts, often called "ohmic" should be free of excess noise. We find that ion implantation followed by thermal annealing leads to

excellent contacts down to 1K and probably lower.⁷ On p-type Ge samples which one does not want to heat, one can apply InGa eutectic to etched surfaces in order to obtain satisfactory contacts.

Fig. 2. Comparison of absorption and photothermal ionization spectroscopy.

2.2 Spectroscopy of the $A_{3,5}$ and A_4 Acceptors

The $A_{3,5}$ and A_4 centers were discovered and can always and only be found in ultra-pure germanium crystals which have been grown in a nitrogen ambient from a melt contained in a graphite susceptor.^{1,7} Such crystals lead to PTI spectra which exhibit the well-known acceptor line series of aluminum and boron. In addition, three further hydrogenic series A_3 , A_4 and A_5 are present. The concentrations of these new acceptors lie in the range of up to $\sim 10^{11} \text{cm}^{-3}$ which is similar to the concentration of residual elemental acceptors (e.g., aluminium). The concentrations of the neutral impurities carbon¹¹ or silicon are typically three to four orders of magnitude higher ($\sim 10^{14}$ to 10^{15}cm^{-3}).

Here we should point out an important feature of the spectra of hydrogenic acceptors. All the bound excited states with p-like wave functions are insensitive to the electronic structure at the core of the acceptor impurity, i.e., they have binding energies which do not depend on the nature of the impurity producing the Coulomb potential. Because photoexcitation occurs only between the s-like ground state and the p-like excited states, one finds that all hydrogenic acceptors exhibit the same set of excited state lines. The position of the set on the wave-number axis depends on the ground state energy of the particular acceptor. This simple situation makes it easy to analyze spectra containing several sets of lines. High resolution, low noise spectra allow the identification of three to over ten lines for each acceptor. This redundancy leads to a high degree of confidence in the results.

At the time of the discovery of A_3 , A_4 and A_5 , no relation between the three series of lines was recognized. Application of uniaxial stress revealed a fundamental difference between the lines belonging to the A_4 series on the one hand, and the A_3 and A_5 series on the other hand. The lines of A_4 series split under stress as one expects for a normal substitutional (fourfold coordinated) acceptor whereas the lines of A_3 and A_5 did not split. The ground state which belongs to the A_4 series has T_8 symmetry while the states leading to the A_3 and the A_5 series cannot be of this same symmetry. They must be either T_6 or T_7 Kramers doublets which do not split under stress. Figure 3 displays two spectra which clearly show the uniaxial stress behavior of aluminum, A_3 , A_4 and A_5 . Further insight into the nature of the new series was gained from the evaluation of the line intensities as a function of temperature. The intensity ratios of corresponding lines of aluminum and of A_4 remain constant over a temperature range from 4.2 to 9K. The ratios of equivalent lines of the A_3 and A_5 series are proportional to a Boltzmann factor $\exp(-E/kT)$ with E corresponding precisely to the shift between the A_3 and the A_5 series ($\approx 1.1\text{meV}$). The ratios of the intensities of the aluminum lines and of the sum of the corresponding A_3 and A_5 lines is again temperature independent. This experimental result unambiguously shows that the A_3 and A_5 line series belong to one center which has a split ground state manifold. The ground state component leading to the A_3 lines is thermally populated from the 1.1meV lower lying ground state component which leads to the A_5 lines. In the chapters which follow, we will refer to the A_4 and the $A_{3,5}$ acceptors.

A further interesting feature of the ground states of A_4 and $A_{3,5}$ is the fact that the splitting of the $A_{3,5}$ ground state is symmetric in regard to the energy of the A_4 ground state.¹² The ground state component leading to the A_3 lines lies 0.55meV above the A_4 ground state while the A_5 lines originate from a state lying 0.55meV below the A_4 ground state. Although the full meaning of this relationship is not understood at the present time, it is a further indication that $A_{3,5}$ and A_4 are closely related.

2.3 Interconversion of A_4 and $A_{3,5}$ and Thermal Annealing

"As grown" crystals contain both the A_4 and the $A_{3,5}$ acceptors. After storage at room temperature for many months we observed that the intensity of the A_4 lines slowly decreased while the $A_{3,5}$ lines increased in relation to the Al lines. A preliminary estimate led to a characteristic time for the room temperature conversion of A_4 into $A_{3,5}$ of the order of ~ 20 months. A brief heating cycle to 670K followed by rapid cooling ($\sim 100\text{K s}^{-1}$) on the other hand showed that all the $A_{3,5}$ lines had vanished while the A_4 center

Fig. 3. Spectra obtained with a Ge sample containing A_3 , A_4 , A_5 , Al and B line series without stress (lower spectrum) and with stress (upper spectrum, $2.5 \times 10^7 \text{ dyne cm}^{-2}$).

had reappeared. The interconversion of A_4 into $A_{3,5}$ and vice versa can reversibly be repeated as long as the sample is not heated for prolonged times at temperatures in excess of $\sim 700\text{K}$. Figure 4 displays two spectra obtained with the same germanium sample after several years of room temperature storage and shortly after heating for six minutes to 673K . Complete conversion from $A_{3,5}$ to A_4 is evident. Quantitative analysis of the two spectra further shows that the intensities of the A_4 lines in the lower spectrum are equal to the sum of the corresponding A_3 and A_5 lines in the upper spectrum to within $\pm 5\%$. This observation is made on all samples containing either only A_4 lines or only A_3 and A_5 lines. It is further evidence that the A_4 and the $A_{3,5}$ acceptors are closely related.

Preliminary interconversion experiments at temperatures between 300 and 700K show that the equilibrium concentrations of $A_{3,5}$ start to decrease monotonically with increasing temperature

beginning around 370K. After equilibration at ~650K, the $A_{3,5}$ lines cannot be detected any longer. The A_4 concentration increases with increasing temperature, complementary to the $A_{3,5}$ concentration. The sum of the two concentrations remains constant over the whole temperature range.

Fig. 4. Spectra obtained with a Ge sample annealed at room temperature (lower spectrum) and heated to 673K (upper spectrum).

Heating to temperatures above ~700K leads to an irreversible exponential decrease of the concentrations of A_4 and $A_{3,5}$.¹³ A typical annealing result obtained at 673K yields an exponential decay time constant of 108hrs. The ir-spectra taken after a 1200hr. annealing cycle contain only aluminum and boron lines. At any point in time during the irreversible annealing of A_4 , one can return to the interconversion regime by

lowering the temperature. This experimental finding suggests that interconversion is not caused by a rapidly diffusing, neutral impurity.

3. SUMMARY AND CONCLUSIONS

The experimental evidence obtained so far indicates that high-purity germanium crystals grown in a pure N_2 ambient from a melt contained in a graphite susceptor contain a novel shallow acceptor center which appears in two forms—either as A_4 or as $A_{3,5}$.

The bound excited states of the center are perfectly hydrogenic. The ground state of the A_4 acceptor is fourfold degenerate with T_8 symmetry. The ground state of the $A_{3,5}$ acceptor is a manifold of which the lowest two components do not split under uniaxial stress. They are Kramers doublets, one with T_6 and one with T_7 symmetry. The two doublets are split by 1.1meV symmetrically above and below the ground state of A_4 . The $A_{3,5}$ acceptor can be thermally converted into the A_4 acceptor and vice versa. The sum of the $A_{3,5}$ and the A_4 acceptor concentrations remains constant as long as the germanium samples are not heated to temperatures above 700K for prolonged times. At high temperatures the novel centers can be irreversibly annealed following an exponential time dependence. The ir-spectroscopy and the interconversion results suggest that we are observing two forms of the same center. We conclude that this novel acceptor center is an impurity complex which contains most probably carbon and nitrogen. The solubility of carbon has recently been determined¹¹ using radioactive ^{14}C . It lies between 10^{14} and $10^{15}cm^{-3}$. To our knowledge, no information is available about the solubility of nitrogen in germanium. We assume that nitrogen occupies interstitial positions because of the small size of the nitrogen atom and because no donor formation has ever been reported in either silicon or germanium. It is unlikely, though it cannot be completely excluded, that oxygen or hydrogen take part in the formation of this center. The concentrations of oxygen and hydrogen are expected to be very low in these crystals. In close analogy to the $A(H,Si)$ and $A(H,C)$ acceptors, we propose that tunneling of one component of the impurity complex leads to the $A_{3,5}$ form of the novel center.

Experiments which should further clarify the symmetry and composition of the novel center are in progress. They include interconversion studies as a function of time of $A_{3,5}$ into A_4 and vice versa, isotopic substitution of ^{14}N with ^{15}N which may lead to a detectable isotope shift in the $A_{3,5}$ ground state splitting¹⁴ and experiments which will help in making an estimate of the solubility of nitrogen in germanium.

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