Germanium-carbide formation on crystal substrate

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Abstract. The formation of microcrystalline germanium-carbide was studied in germanium crystal substrate using a nuclear technique called perturbed γ-γ angular correlation (PAC). Carbon atoms were incorporated in the host matrix by implantation and, consequently, several carbon related complexes were detected after annealing the sample at various temperatures in vacuum. Information about the local environment of the probe atoms can be obtained via the interaction between carbon and unstable probe nucleus (^{111}In). At high dose carbon implantation two defect complexes have been identified via unique nuclear quadrupole interaction frequencies; ν_{Q1} = 207(1) MHz (η = 0.2) and ν_{Q2} = 500(1) MHz (η = 0), respectively. Which are attributed to two different types of carbon-indium pairs in the substrate lattice. The orientations of the measured electric field gradients and the thermal stability of the defect complexes are studied. The results are encouraging towards attaining germanium carbide crystal which has attractive potential for applications.

1. Introduction

Germanium-carbide has increasingly become the focus of research attention because of its potential application in the field of electronics and high temperature devices. The realization of large size crystal is one of the major challenges in this study because of the significant difference in atomic sizes of germanium and carbon atoms which is hindering the crystal growth. In fact, carbon is one of the residual impurities in many semiconducting materials which is often unavoidable in material processing [1, 2, 3, 4, 5, 6, 7]. Among many of its applications important to the current discussion is that carbon is used to compensate strain in SiGe compound semiconductor. The PAC method was employed in the past to study carbon related complexes in silicon with the view to identify carbon in silicon but, it was not materialize the detection of observable interaction frequency in silicon Ott et al [3] partly due to high oxidation rate and fast diffusion of carbon in silicon. However, the formation of In-C complex in silicon was reported using infrared spectroscopy measurements which prompted us to search for a new In-C pair in germanium substrate using PAC. This should be possible given the fact that silicon and germanium atoms share the same chemical properties. Until recently much attention was not given in the formation of Ge-C system, because of the very low solubility (10^8cm^{-3} -10^{10}cm^{-3}) [5] of carbon in germanium. However, using the electron cyclotron resonance (ECR) plasma processing method; Herrold et al.[1] were able to grow microcrystalline thin film of germanium-carbide on different substrates up to 2% carbon concentration. The newly grown germanium-carbide is reported to have 1.1eV energy band gap, very close to that of silicon, depending on the carbon concentration [1]. This is a very important progress towards attaining crystalline germanium-carbide, which has promising electrical and optical properties. In this work, carbon

was incorporated into germanium by high dose implantation and, subsequently, we observe the lattice locations of the solute atoms at different annealing temperatures.

2. Experimental Details

Perturbed γ-γ angular correlation (PAC) utilizes unstable radio active probe nucleus (^{111}In) to investigate the microscopic environment of the atoms in the host matrix. The probe atom (^{111}In) populates by way of electron capture process (EC) to an excited state of ^{111}Cd ($t_{1/2}$ = 84ns). Hence, the time spectra are measured from the depopulation of the excited state of ^{111}Cd to a stable atom by successive emission of two γ-rays. The γ-rays are measured in coincidence, and hence a proper combination of the coincidence time spectra leads to the so called ratio function R(t) which carries information about the interaction. The interaction between the nuclear quadrupole moment of ^{111}Cd intermediate state and the surrounding electromagnetic field provides information about the environments of the probes. Therefore, the electric field gradient (EFG) characterizing the probe environment is the second derivative of the electric potential caused by the surrounding charges. In the principal axes system, the diagonalized field tensor constitutes three diagonal elements V_{xx}, V_{yy} and V_{zz} with the convention $|V_{xx}| \leq |V_{yy}| \leq |V_{zz}|$. The principal component of the EFG tensor (V_{zz}) can be obtained from the measured quadrupole interaction frequency (QIF) and the asymmetry parameter $\eta = (V_{xx}\text{-}V_{yy})/V_{zz}$. Details of the PAC method are available in many papers and text books[8, 9]. The most important parameters of the hyperfine interaction can eventually be determined by comparing R(t) with an appropriate perturbation function as:

$$R(t) = A_{22} \sum_i f_i G^i_{22}(t) \tag{1}$$

If there are several distinct sites having fractional populations f_i of the probe nuclei at a unique environment i, the average perturbation function is :

$$G^i_{22}(t) = \sum_{n=0}^{3} S^i_n \cos(g_n(\eta)\omega^i_0 \cdot t) \exp[-g_n(\eta)\omega^i_0 \delta^i \cdot t] \tag{2}$$

where ω_0 = (3/10)eQVzz/h is the fundamental precession frequency of the interaction. The quadrupole moment (Q) of the probe nucleus has a magnitude Q(5/2+) = 0.83(13)b [8] for an isomeric state of ^{111}Cd. The Sn (θ_j, η) coefficients carry inormation about the orientation of V_{zz}, which depends on the geometry of the detectors and described by the Euler angles θ_j [8]. The time spectra taken from probe atoms that are decorated with defect will be modulated by characteristic triple interaction frequencies ω_1, ω_2 and ω_3.

Germanium samples were obtained from CZ grown germanium crystal wafer with $< 100 >$ surface, and are cut to the size of 6x5 mm^2. The implantations were carried out in two steps, first the indium isotope (^{111}In) was implanted at 160 keV with doses ranging between 10^{12} and 10^{13} atoms/cm^2 in different samples. This creates an implantation profiles centered at (52 $\pm$ 16)nm in germanium according to transport of ions in matter (TRIM) simulation. After substantially reducing the radiation induced damage by thermal annealing in vacuum ($\sim 10^{-6}$mbar), the samples were once again implanted with carbon at 40 keV with different implantation doses ranging between (1-5)x10^{15} atoms/cm^2. Finally, the time spectra were taken at room temperature after each vacuum annealing steps in a five minutes holding time.

3. Results Discussion

Fig. 1(a) shows the PAC time spectra taken after annealing the sample at the various annealing temperatures. The sample was initially suffered from radiation induced damaged but slowly recrystalize after each annealing steps. The first sign of crystal re-growth can be observed after annealing the sample at 450°C (panel 1 of Fig. 1(a)). The PAC signals are then gradually

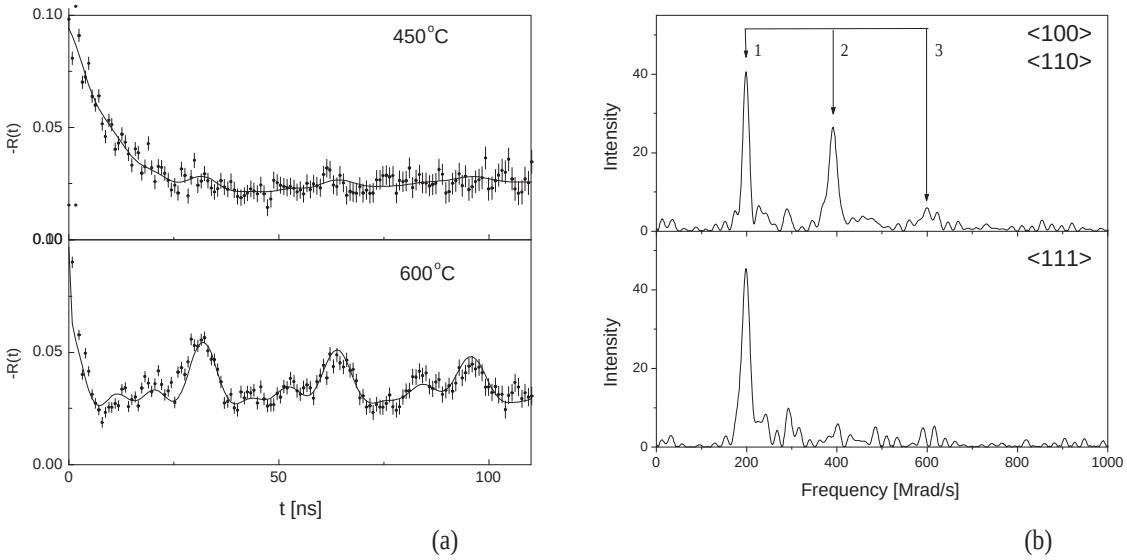

Figure 1. (a) PAC time spectra of the In-C complex in germanium, and the solid lines are the least square fits to the data according to Eq.1. (b) The Fourier transform of the time spectra measured after annealing the sample at 600°C.

modulated by an interaction frequency of $\nu_{Q1} = 207(1)$ MHz ($\eta = 0.16(3)$) (panel 2 of Fig. 1(a)). This quadruple interaction frequency represents well defined and unique environment of the probe atom in the host lattice. In fact, it is associated with the existence of carbon in germanium, since such frequency has never been observed in germanium even in the presence of other impurities. The amplitude of modulation increases with temperature showing the population growth of the defect complex in the sample. The spectra are followed by large frequency damping of $\delta_1 = 1.7(6)$ and $\delta_2 = 1.5(4)$ at 550°C and 600°C, respectively. Such damping factors show the wide distribution of the frequency around a maximum, and is a clear indiction of the structural non-uniformity of the host matrix; where probe atoms take sites of the same lattice environment but accompanied by different neighborhoods. The decreasing tendency of the frequency damping with temperature suggests the recovery of the radiation induced damage near the defect complexes. On the other hand, another new interaction frequency of $\nu_{Q2} = 500(1)$ MHz and ($\eta = 0$) emerged in the place of the former after annealing the sample above 600°C. This frequency of course represents a new probe environment in the sample which has been thoroughly discussed elsewhere [10] and do not represent the formation of crystal germanium-carbide. Furthermore, in an effort to determine the lattice location of carbon in the complex detected at $\leq$ 600°C; we measured the PAC time spectra ($\propto V_{zz}$) with respect to the three major crystal axes, namely $< 100 >, < 110 >$ and $< 111 >$, respectively. The orientation of (V_{zz}) in the host matrix would in fact suggest the possible location of the carbon next to the probe atom. Fig. 1(b) is the Fourier transform of the time spectra measured along the three major crystal axes after annealing the sample at 600°C. The first panel of the figure shows three transition frequencies (1, 2 and 3) of the quadrupole interaction of the probe nucleus with the surrounding extranuclear fields. The peaks amplitudes distinctly show that the frequency is indeed the first interaction frequency ($\nu_{Q1} = 207(1)$ MHz) observed in the time spectra and represented by site 1. The amplitudes of the peaks 2 and 3 vanish when the detectors are aligned with the $< 111 >$-crystal axis (panel 2 of Fig. 1(b)) suggesting the orientation of the principal

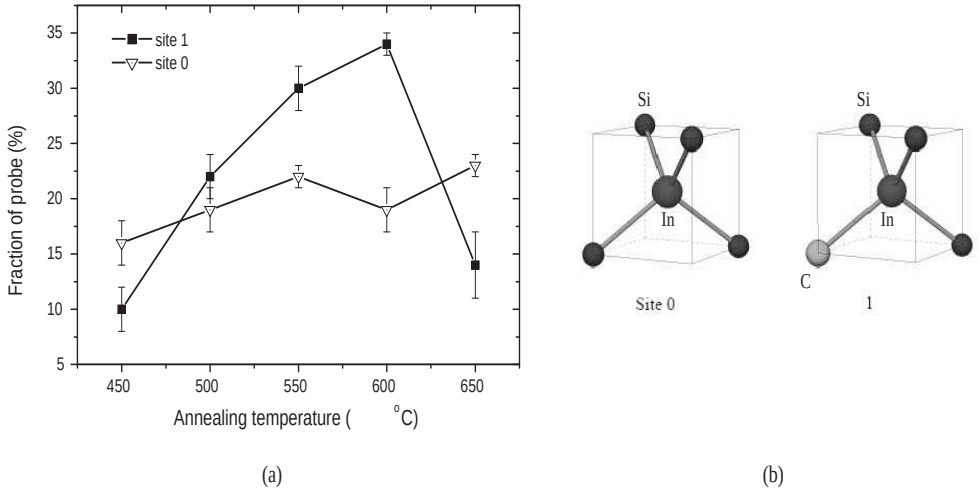

Figure 2. Fraction of probe atoms situated as site 0 and site 1 at different annealing temperature.

component of the field gradient tensor (V_{zz}) be along the $< 111 >$-crystal axis. This orientation of the V_{zz} would indicate that the possible location of carbon in the complex might be the substitutional site next to the probe atom in diamond type structure of germanium.

Fig. 2 shows the fractional population of two different probe environments in the sample namely site 0 and site 1 respectively. Though the amplitude of the frequency modulation is small for time spectra taken below 450°C, but there exists a small fraction of probe atoms in unique lattice locations. For instance, nearly 16(2)% of the implanted probe atoms were detected at undisturbed sites (site 0) while another 10% of the probe were decorated with carbon related complex (site 1) after 450°C. The population of site 1 grows monotonically with temperature and reaches maximum of $f_1 = 34(2)\%$ at 600°C. However, as the temperature exceeds the 600°C mark the population of site 1 drastically decreases and drops nearly to 12(3)% at 650°C. The complex eventually vanishes from the spectrum at 700°C. In all the time spectra, we measured the substantial fraction of the probe atoms at non-unique lattice sites that can not be resolved by the present PAC apparatus. Above 450°C annealing temperatures, the best fits to the data are obtained by taking into account nearly $f_p = 48(5)\%$ of the probe atoms to be linked with lattice sites having highly disturbed environments. These sites could be associated with several carbon clusters (precipitates) which are formed as the result of different chemical and/or thermal interactions with the probes in the host lattice.

An interesting similarity is observed on the population of substitutional carbon detected by PAC on one hand, and ion channeling and infrared absorption methods on the other [1]. According to the latter substitutional carbon atoms are observed after annealing the sample above 350°C; they are then depopulated from these sites at high temperatures and eventually disappears at 700°C. The report also indicated that maximum of 31(3)% of the implanted carbon was found at substitutional lattice sites while the remaining 69(3)% are randomly located in the substrate lattice. In PAC, an indium-carbon complex (site 1) is detected below 650°C annealing temperatures. The largest population of this complex is 34(2)% of the probe atoms (Fig. 2(a)). Therefore, comparing the ranges of temperature where the substitutional carbon is observed by ion channeling and infrared absorption on the one hand and the detection of site 1 by PAC (Fig. 2) on the other. We found similar ranges, in which all three methods are able to

detect the occurrence of well-defined structural site of carbon in germanium. According to these information, it is possible to conclude that site 1 with an interaction frequency Q = 207(1) MHz is the result of the interaction of indium with substitutional carbon in germanium. Despite the limitation of PAC to only the population of the probe atoms, the present results clearly show the formation of substantial amount of isolated substitutional carbon in germanium below 650°C.

4. Conclusion

Carbon related complexes have been observed using PAC method after high dose carbon implantation in germanium which are characterized by different lattice locations of the solute atoms in the host lattice. Significant population of isolated substitutional carbon are observed below 650°C annealing temperatures. However, the majority of the implanted carbon possesses disordered lattice environment where nearly 50% the probe atoms are trapped. The observed properties of site 1 matches the properties of substitutional carbon reported by ion channeling and infrared spectroscopy in germanium. It is therefore possible to conclude that microcrystalline germanium-carbide has been formed in germanium substrate after high dose carbon implantation followed by annealing at 600°C.

Acknowledgments

The author wouldlike to acknowledge the assistance of all staffs working in the Mass-Separator facility of the Helmholtz-Institut für Strahlen-und Kernphysik (HISKP)of the University of Bonn, Germany. He thanks members of the material science research group of the HISKP for the constructive suggestions in the preparation of this work.

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