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EFFECT OF PRESSURE ON ARSENIC DIFFUSION IN GERMANIUM

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ABSTRACT

We report preliminary results of a study of the activation volume for diffusion of arsenic in germanium. High-temperature high-pressure anneals were performed in a liquid argon pressure medium in a diamond anvil cell capable of reaching 5 GPa and 750° C, which is externally heated for uniform and repeatable temperature profiles. The broadening of an ion-implanted arsenic profile was measured by Secondary Ion Mass Spectrometry. Hydrostatic pressure retards the diffusivity at 575° C, characterized by an activation volume that is +15% of the atomic volume of Ge. Implications for diffusion mechanisms are discussed.

INTRODUCTION

Bulk diffusion in crystalline solids is mediated by point defects, such as vacancies in metals. The diffusivity can be perturbed by changing the equilibrium concentration of point defects with hydrostatic pressure. High pressure typically reduces the diffusion constant in metals, suggesting a vacancy mechanism for diffusion [1-3]. High pressure techniques can also be used to study the defects mediating diffusion in semiconductors. The slow rate of diffusion in elemental semiconductors however, requires very high temperatures to achieve measurable diffusivities. High temperature, high pressure devices suitable for these experiments have proved difficult to make. Werner *et al* [4] used a compressed gas cell to measure the activation volume of self diffusion of germanium in intrinsic and doped germanium. However they were limited to a maximum pressure of 0.6 GPa. In this paper we report preliminary results of a technique capable of attaining much higher pressures with less risk of contamination, applied to the diffusion of arsenic in germanium.

The diffusivity of a random-walking species in a cubic system is:

$$D = \frac{1}{6} \lambda^2 \Gamma \quad (1)$$

where λ is the jump distance and Γ is the jump rate. In the transition state theory [5] the jump rate is:

$$\Gamma = P \nu \exp(-\Delta G_m / kT) \quad (2)$$

Fig. 1. Standard free energy vs. system configuration as atom jumps across barrier to new position. ΔG_m is the barrier to migration.

where ΔG_m is the free energy of migration v is the attempt frequency, kT has the usual meaning and P is the probability that there is a defect in a position for the jump to take place. Assuming random site occupation, the probability that the defect exists next to the jump site is:

$$P = \exp(-\Delta G_f^0/kT) \quad (3)$$

where ΔG_f^0 is the standard free energy of formation the defect in the process depicted in Fig. 2.

Fig 2. Vacancy Formation

The final form the diffusivity is:

$$D = av\lambda^2 \exp(-\Delta G^*/kT) \quad (4)$$

where $\Delta G^* = \Delta G_f^0 + \Delta G_m$ and a is a geometrical factor that takes into account the crystal structure and the diffusion mechanism [6].

The familiar activation enthalpy comes from the dependence of ΔG^* on reciprocal temperature. The activation volume comes from the dependence of ΔG^* on pressure using the thermodynamic identity

$$V = \left. \frac{\partial G}{\partial P} \right|_T, \quad (5)$$

which, when applied to Eq. (4), yields

$$\Delta V^* = -kT \left. \frac{\partial \ln D}{\partial P} \right|_T + kT \left. \frac{\partial \ln(av\lambda^2)}{\partial P} \right|_T \quad (6)$$

where ΔV^* is the activation volume. The second term is has been shown to be small [4]. Hence the activation volume is determined experimentally by a measurement of the pressure-dependence of the diffusivity:

$$\Delta V^* \approx -kT \left. \frac{\partial \ln D}{\partial P} \right|_T \quad (7)$$

and

$$\Delta V^* = \Delta V_f^0 + \Delta V_m \quad (8)$$

where ΔV_f^0 , the formation volume, is the volume change in the system upon formation of one defect in its standard state. ΔV_m , the migration volume, is the additional volume change when the defect reaches the saddle point in its migration path.

For the above analysis we have assumed that the defects are in thermodynamic equilibrium at the temperatures and pressures under which the experiment is conducted. If the time scale of the experiment is too short for the defects to equilibrate, then the volume of migration term will become disproportionately important. For example, in the extreme case where the concentration of defects is constant, the measured activation volume will be equal to the volume of migration.

EXPERIMENTAL METHOD

The experimental procedure is to anneal germanium samples with known initial arsenic depth profiles at various pressures for a fixed temperature. Diffusion is measured *ex situ* by sputter sectioning using Secondary Ion Mass Spectrometry (SIMS).

Samples are prepared by ion implantation of As^+ at 500 keV with a dose of 2×10^{14} ions/cm² at 77 K into Ge (100) wafers 50 μm thick. The resultant depth profile of As is shown by SIMS to be approximately gaussian in shape with a peak concentration of 7×10^{18} atoms/cm³ at 215 nm depth, with a FWHM of 67 nm. The wafers are subsequently implanted at 77 K with $^{71}\text{Ge}^+$ at 250 keV to a dose of 5×10^{14} ions/cm² and at 500 keV to a dose of 8×10^{14} ions/cm², in order to completely amorphize the implanted layer which is necessary for the subsequent restoration of defect-free crystal by Solid Phase Exptaxial Growth (SPEG). SPEG occurs at temperatures too low for measurable diffusion to occur; we found that approximately 15 minute anneals at 450° C restores crystallinity in our samples [7]. The samples are then cleaved into small pieces approximately 150 μm by 150 μm to fit into the Diamond Anvil Cell (DAC). Diffusion anneals were for various pressures at 575 degrees C for 30 minutes.

Fig 3. Pressure Chamber in Diamond Anvil Cell

The high pressure device is a modified Merrill-Bassett [8] DAC. The cell body is constructed from Haynes 230, a nickel based superalloy. The pressure is generated by forcing two diamonds together on a metal 'gasket' with a hole in it, which serves as a pressure chamber (Fig 3). The

gasket deforms plastically, simultaneously forming a seal and the chamber walls. We use rhenium as a gasket material due to its high strength and ductility at both ambient and high temperature. The pressure chamber is loaded cryogenically with liquid argon as a pressure transmitting medium. Liquid argon is both chemically inert and hydrostatic because it does not solidify until 7 GPa at 575° C, the temperature of our experiment. The cell is externally heated in an inert atmosphere. The furnace has an optical window for *in situ* pressure measurement.

Pressure is measured using fluorescence peak shifts of samarium doped yttrium aluminum garnet (Sm:YAG). Typically pressure is measured in a DAC by using ruby fluorescence peak shifts, but these peaks are not visible beyond about 250° C. Hess and Schiferl [9] have shown that Sm:YAG may be used to measure pressure at least up to 800° C. The Sm:YAG is excited by the 488 nm line of Ar ion laser. The spectrum is acquired using a spectrometer and a diode array. Pressure was calculated by simultaneously fitting the 617 nm, 616 nm and 610 nm lines. The fit was based on Hess and Schiferl's calibration of the 617 nm and 616 nm lines. The 610 nm line was calibrated against the other two at room temperature and ambient pressure. By assuming that the temperature and pressure shifts add linearly we developed a protocol for fitting all three lines. This procedure was necessary for robust and repeatable fits of the Sm:YAG spectrum.

Fig. 4. Arsenic depth profiles for two samples annealed at different pressures for identical temperatures and durations.

Diffusion is measured by Secondary Ion Mass Spectroscopy (SIMS). We used a VG Ionex 1170X magnetic sector SIMS. The primary beam was 16 keV Cs⁺, rastered to produce a flat crater bottom. To remove crater wall effects, the secondary ions were collected from an area that was gated electronically to cover only the central 5% of the area of the crater. The AsGe⁻ ion, which has a stronger signal than the As⁻ ion, was tracked for the arsenic concentration profile. The as implanted depth profiles are gaussian within our experimental resolution. Typical profiles are shown in Fig. 4. The top 100 nm of the profiles are lost due to a surface transient artifact of

SIMS. The amount of diffusion was determined by fitting gaussians to the broadened depth profiles, using a no-flux boundary condition at the surface. The solid curve in Fig. 4 is a fit to the 3.5 GPa anneal and it gives a diffusivity of 1.5×10^{-14} cm²/sec. The dashed curve is a fit to the 0.1 GPa anneal and gives a diffusivity of 3.7×10^{-14} cm²/sec. Pressure clearly reduces the diffusivity of As in Ge.

RESULTS

We summarize our preliminary results in Fig. 5. The error bars on the point at 2.0 GPa are unusually large because the SIMS primary beam spontaneously changed its intensity in mid-profile, reducing the depth calibration accuracy. A least-squares fit of Eq. (7) to the data yields ΔV^* to be $+2.0 \pm 1.0$ cm³/mole, which is $15\% \pm 7\%$ of Ω_{Ge} , the atomic volume of germanium.

Fig. 5. Diffusion of As in Ge vs. pressure for 30 minute anneals at 575 degrees C

DISCUSSION

We have found $\Delta V^* = +0.15 \Omega_{\text{Ge}}$ for As diffusion at 575° C. Dopant diffusion in Ge is generally believed to occur by a vacancy mechanism [6]. The vacancy formation volume has been calculated in Si, and various calculations result in formation volumes (ΔV_f^0) between $+0.75 \Omega_{\text{Si}}$ and $+1.1 \Omega_{\text{Si}}$ [10-14]. One might then expect a similar sized formation volume for vacancies in germanium, in which case Eq. (8) would imply a migration volume of about $-0.6 \Omega_{\text{Ge}}$ to $-0.95 \Omega_{\text{Ge}}$ for the Ge vacancy. Negative migration volumes for point defects in covalent networks are consistent with the effects on pressure on SPEG of Si and Ge [15,16], and the interdiffusion of amorphous Si-Ge multilayers [17]. Our result would then be consistent with a

vacancy mechanism if the vacancy mobility is enhanced by pressure, but not as strongly as the vacancy concentration is reduced by pressure.

Werner *et al* [4] found ΔV^* for self diffusion in intrinsic germanium to vary from $0.24 \Omega_{\text{Ge}}$ at 603°C to $0.41 \Omega_{\text{Ge}}$ at 803°C . Combined with the effects of doping on self diffusion they concluded that self diffusion in Ge is mediated by two charge states of vacancies, and inferred activation volumes of $+0.28 \Omega_{\text{Ge}}$ for the negatively charged vacancy and $+0.56 \Omega_{\text{Ge}}$ for the neutral vacancy. They do not separate the migration and formation components of the activation volume. Note that as a donor the arsenic atom in our study will be positively charged and will tend to associate with the negatively charged vacancy, which has the smaller activation volume. Work is in progress to determine whether the defect concentrations are in equilibrium during these experiments, by repeating the experiments at the same temperatures for significantly longer times. If the defect concentrations are in equilibrium then there should be no change in the apparent diffusivity with time.

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