Effect of Pressure on Arsenic Diffusion in Germanium: Evidence Against Simple Vacancy Mechanism

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We have measured the effect of pressure on As diffusion in Ge. Diffusion anneals on ion-implanted samples were carried out in a high temperature diamond anvil cell using fluid argon as a clean, hydrostatic pressure medium. At 575 °C over the pressure range 0.1 to 4 GPa, pressure slightly enhances the diffusivity, characterized by an activation volume of -1.7±1.4 cm³/mole or -0.12±0.10 times the atomic volume of Ge. The results call into question the prevailing view that diffusion of group III, IV and V elements is mediated entirely by vacancies. Potential explanations of these results are discussed.

Because understanding and controlling diffusion related phenomena become increasingly important as semiconductor device dimensions decrease, diffusion in semiconductors has been heavily studied. Despite this emphasis there remains no consensus about the relative roles of the various proposed mechanisms for diffusion of many group III, IV, and V elements in Si. Diffusion of these elements in Ge is commonly believed to be mediated entirely by vacancies, but this perception is based on few experimental studies [1,2]. The increasing importance of Ge for uses such as in Si1-xGex devices necessitates further study of diffusion in Ge.

The effect of pressure, \( p \), on the diffusivity, \( D \), is characterized by the activation volume, \( \Delta V^* \):

\[
\Delta V^* = -kT \left( \frac{\partial \ln D}{\partial p} \right)_T ,
\]

when negligible correction terms are neglected [3]. \( \Delta V^* \) can be either positive or negative, depending upon whether \( D \) decreases or increases with \( p \), respectively. For a point defect mechanism, \( \Delta V^* \) is normally the sum of two components:

\[
\Delta V^* = \Delta V_f + \Delta V_m ,
\]

where \( \Delta V_f \), the formation volume, is the volume change in the system upon formation of a defect in its standard state, and \( \Delta V_m \), the migration volume, is the additional volume change when the defect reaches the saddle point in its migration path. The formation volume characterizes the pressure-dependence of the equilibrium point defect concentration while the migration volume characterizes the pressure-dependence of the defect mobility.
Unlike activation energies, which are always positive, activation volumes are expected to have different signs for different types of point defect mechanisms. Hence a measurement of the activation volume can be a more revealing test for distinguishing between potential diffusion mechanisms. Before our study [4], the only published measurement of $\Delta V^*$ for diffusion in Ge was that of Werner et al. for self-diffusion [5]. In silicon there are a few more such measurements [6-8].

Samples were prepared by ion implantation and Solid Phase Epitaxial Growth (SPEG) as described elsewhere [4]. Diffusion anneals were carried out for various pressures at 575 °C in a Diamond Anvil Cell described elsewhere [4,9] and loaded cryogenically with liquid argon as a clean, hydrostatic pressure transmitting medium. The cell is externally heated in an inert atmosphere in a furnace with a window for optical access. The new discovery that makes this technique possible is the real-time in-situ pressure measurement using the fluorescence peak shifts of Sm doped Yttrium Aluminum Garnet (Sm:YAG) [4,9,10].

Diffusion is measured ex situ by sputter sectioning using Secondary Ion Mass Spectrometry (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 depth profile. The implanted profile is gaussian within our experimental resolution. 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 image profiles at negative depth to account for the reflecting wall at the surface. Fig. 1 shows typical profiles.

Using Eq. (1) $\Delta V^*$ was calculated by fitting a straight line to the points in Fig. 2. The result is $\Delta V^* = -1.7 \pm 1.4 \text{ cm}^3/\text{mole} = -0.12 \pm 0.10 \Omega_{\text{Ge}}$, where $\Omega_{\text{Ge}}$ is the atomic volume of Ge at standard T and p. The fit was performed using a weighted linear least squares technique. The greater amount of scatter at low pressure is because much of the low pressure data were collected early on in the study, before the experimental techniques had been fully refined. Additionally, we expect greater uncertainties for lower measured diffusivities, as the amount of broadening will be closer to the detection limit. For comparison, slopes for activation volumes of $\pm 0.5 \Omega_{\text{Ge}}$ and $\pm 1.0 \Omega_{\text{Ge}}$ are also shown in Fig. 2. If diffusion is point defect mediated, Eq. (2) is invalid if the point defect concentrations do not maintain their equilibrium levels for the pressures and temperatures of the experiment. The independence of $D$ on anneal duration is evidence that equilibrium concentrations are maintained in this experiment [9].

In Table I we compare our measured activation volume [4] with that of Werner et al [5] for Ge self diffusion under various conditions and those of Lu et al [11] for SPEG in Ge. By measuring the effects of dopants on self diffusion and modeling the dependence of the charged vacancy concentration on the Fermi level (assuming all other parameters, such as jump rates and activation volumes are invariant), Werner et al. also determined that the negative vacancy is responsible for 77% of the transport for self-diffusion in Ge at 700 °C.

We now discuss the implications of these results for possible diffusion mechanisms. We first show that it is difficult to reconcile the simple vacancy mechanism with the measurements. We then discuss other possible mechanisms, although these data do not permit a critical test of them.
Figure 1. Depth profiles and gaussian fits.

Figure 2. Activation volume plot at 575 °C.
Let us consider the possibilities for the relative contributions through Eq. (2) of formation and migration terms to the measured activation volume for a 100% vacancy mechanism. Werner et al. assumed that $\Delta V_m$ is small and used their measured $\Delta V^*$ as an approximation for $\Delta V_f$. With this they concluded that the vacancy is the predominant point defect mediating self diffusion. If we likewise assume $\Delta V_m$ to be negligible, our results imply $\Delta V_f = -0.12 \Omega_{Ge}$. This value is close to that expected for a direct interchange mechanism [12] because it does not involve a point defect and consequently $\Delta V_f = 0$. Werner et al. base their assumption of small $\Delta V_m$ on studies of self diffusion in gold [13]. The assumption may not be valid for Ge.

Lu et al. measured large negative $\Delta V^* = -0.46 \Omega_{Ge}$ for SPEG and suggested that their value is approximately equal to $\Delta V_m$. Such large negative $\Delta V_m$ values can be rationalized for covalent network materials [14]. If we assume that the atomic transport processes of SPEG and diffusion in tetrahedral covalent networks have similar $\Delta V_m$ values as large and negative as $\Delta V_m = -0.4 \Omega_{Ge}$ must then be considered plausible for diffusion in Ge. In this case $\Delta V_f = +0.3 \Omega_{Ge}$. Such a small formation volume implies a very large inward relaxation around the vacancy. For comparison, ab-initio calculations [15] for Si give a formation volume of $+0.75 \Omega_{Si}$ and we currently have no reason to expect such a large difference between $\Delta V_f$ in Si and Ge.

Finally if we assume $\Delta V_f = +0.75 \Omega_{Ge}$ in accordance with the theoretical result for Si then our experiment implies $\Delta V_m = -0.87 \Omega_{Ge}$. The difference between the enthalpy of migration at zero pressure ($\Delta E_m$) and at high pressure ($\Delta H_m$) is $p\Delta V_m$ (assuming $\partial V_m/\partial p$ to be negligible). In Si, $\Delta E_m$ for vacancies ranges from 0.18 to 0.45 eV for different charge states [16-19]. Scaling with the bond strength ratios gives expected $\Delta E_m$ in Ge of 0.14 to 0.36 eV. When $p\Delta V_m$ is added to these values, the migration enthalpy vanishes at a critical pressure of $p_{crit} = \Delta E_m/\Delta V_m = 1.2$ to 3.0 GPa. At $p_{crit}$ we expect some kind of break in the slope in Fig. 2 as the barrier to migration vanishes, precluding a further reduction in the barrier height with increasing $p$. Such a break is not observed.

Fig. 3 graphically summarizes these arguments. The permitted combinations of $\Delta V_f$ and $\Delta V_m$ lie within the diagonal band. Assuming $\Delta E_m < 0.36$ eV and, from Fig. 2, $p_{crit} > 3.5$ GPa requires that $\Delta V_m > -0.73 \Omega_{Ge}$. Thus we exclude the cross-hatched region below the horizontal line. The expected formation volume, indicated by the vertical line, intersects the diagonal band just barely in the excluded region. If diffusion is mediated entirely by vacancies then either the vacancy formation volume must be lower than expected or the migration energy must be greater than expected. Experimental studies are currently under way to raise the lower limiting value of $p_{crit}$ in Fig. 2, which would in turn raise the horizontal line bounding the excluded region in Fig. 3.
Multiple diffusion mechanisms may be operating in parallel. By comparing our data with calculated activation plots for a pair of diffusion mechanisms operating in parallel we have determined that our data are inconsistent with a double defect mechanism where the activation volumes are large and of opposite signs [9]. Two mechanisms, however, with opposite-signed activation volumes of magnitude less than about 0.4 $\Omega_{\text{Ge}}$ and the right ratio of pre-exponential factors cannot be ruled out by the data.

The large positive $\Delta V^*$ of Werner et al. is the principal evidence for the predominance of the vacancy mechanism for self diffusion in Ge. They also show that the negative vacancy, $V^-$, is predominant. Donors such as As should be positively charged and should bind to $V^-$. (This is indeed the case in Si [1,20]). The much faster diffusion of donors than acceptor and self-diffusion in Ge [1] has been attributed to $\text{As}^+ - V^-$ association [2,21]. Because donors raise the Fermi level, the predominance of $V^-$ is further enhanced. However, in diamond cubic structures the increased association of a vacancy with an impurity atom due to binding may not cause a large increase in the impurity diffusivity by the normal vacancy mechanism, because nearest neighbor sites do not share any other nearest neighbors and therefore the pair must dissociate in order to migrate. Binding therefore causes an offsetting reduction in the correlation factor [22]. We note that this reduced correlation factor does not apply to delocalized or "extended" vacancies [23] or if significant binding still exists between vacancy and impurity in third-neighbor locations [22]. It is not yet known into which category falls the case at hand.

![Figure 3. Permitted values of formation and migration volumes for simple vacancy mechanism.](image-url)
Finally, it should be noted that if the correlation factor for impurity diffusion is reduced by defect-impurity binding then a significant volume change upon binding will add a correction term to eq. (2), just as a significant enthalpy change upon binding will add a correction term to the corresponding equation for activation enthalpies [22].

We now consider other mechanisms. If the interstitialcy mechanism predominates for arsenic diffusion then there must be some explanation why it is not the predominant mechanism for self-diffusion. One suggestion due to Frank [24] is that negative interstitials may be mediating As diffusion in Ge. Association with negative interstitials might then enhance significantly the diffusion of donors compared to self diffusion and also explain a non-positive \( \Delta V^* \) for As diffusion while maintaining a large, positive \( \Delta V^* \) for self diffusion.

It is also possible that a vacancy mechanism is operating with jumps between lattice sites that are not nearest neighbors. In Ge, second-neighbor jumps of As or Ge would permit long-range transport of As without As\(^+\)-V\(^-\) dissociation, and ball-and-stick modeling of the midpoint of the migration path, shown schematically in Fig. 4, indicates that a large negative migration volume is plausible [25]. However calculations of the energetics and volumetrics involved are required to check the feasibility of such mechanisms.

A suggestion due to Gösele [26] is that arsenic may be diffusing in Ge via a Frank-Turnbull dissociative mechanism. If the predominant effect of pressure is to reduce the vacancy concentration, thereby increasing the mean diffusion distance before recombination of an interstitial arsenic and a vacancy, then the activation volume would be negative. It might appear that the energy cost for an arsenic atom jumping off a lattice site and becoming interstitial is prohibitive. However, if the vacancy and interstitial truly dissociate then this energy cost is split among two point defects — i.e., you get twice the entropy as for a single defect and so the energy/entropy balance is the same as for creating a single point defect at half the formation energy.

![Figure 4. (a) Tarzan mechanism involving second-neighbor vacancy jumps permits long-range transport of bound As\(^+\)-V\(^-\) pair without dissociation. Filled circle: As\(^+\); open circles: Ge. (b) Potential saddle-point configuration with negative migration volume [25].](image-url)
In summary, the small, negative activation volume for As diffusion calls into question the prevailing view that diffusion of group III, IV and V elements is mediated entirely by a normal vacancy mechanism in Ge. If diffusion of As is mediated entirely by vacancies then either the vacancy formation volume is unexpectedly low or the energy of vacancy migration is unexpectedly high. The interstitialcy and direct interchange mechanisms cannot be ruled out. Accurate calculations of the energetics and volumetrics of formation and migration of various defects would be very helpful.

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REFERENCES
a) Present address: Charles Evans and Associates, 301 Chesapeake Dr., Redwood City CA USA 94063.
24 W. Frank, (private communication, 1994).