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Effect of Grain-Boundaries on the Solubility of Copper in Silicon*

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Solubility studies of copper in high-purity vapour-grown polycrystalline silicon have given direct evidence for strong solute-atom/grain-boundary interactions in this system. The interaction energy between copper-atoms and grain-boundaries was ascribed to chemical bonding and was determined to be −1.47 ± 0.04 eV. Since the grain-structure of the vapour-grown material was found to be very complex, a precise determination of the actual grain-boundary solubility was not possible. A theoretical calculation based on enthalpic considerations (neglecting changes in thermal entropy) estimated the ratio of the grain-boundary solubility to the single-crystal solubility to be $\simeq 4 \times 10^6$ at 700° C.

1. Introduction

A basic understanding of solute-atom/grain-boundary interactions is technologically important. Solute segregation to grain-boundaries, for example, is often responsible for inhibition of recrystallisation and grain-growth. In many instances segregation results in embrittlement and corrosion susceptibility. The electronic properties of polycrystalline materials may also be affected by such interactions.

Solute-atoms interact with grain-boundaries in a manner not dissimilar to the way they interact with dislocations. This is evident if one considers that a low-angle grain-boundary can be constructed from an array of dislocations. The physical nature of high-angle grain-boundaries is not yet defined by a complete theory; however, it is generally believed that they have a random misfit structure resembling a liquid, and are not more than three atomic diameters wide [1]. The thermodynamic difference between a grain-boundary and the interior of a homogeneous phase is due to the surface tension that exists at an interface. Solute elements which decrease the surface tension should therefore tend to adsorb on the interface. The effect of solutes on grain-boundary tension is difficult to treat theoretically, however, so recourse is usually made to the statistics of occupancy of solute-atoms in distorted and normal lattice regions.

2. Theoretical Considerations

Following McLean [2], the equilibrium solute concentration in a distorted region of a lattice may be related to the concentration in a normal region (measure of the degree of grain-boundary segregation) by determining the Gibbs free energy, G, of the solute-atoms which are distributed among N undistorted sites containing N_1 solute-atoms and n distorted lattice sites containing n_1 solute-atoms. If the enthalpies of the solute-atoms in undistorted and distorted sites are H_1 and $H_1{}^b$ (both assumed independent of concentration) respectively, then the free energy of the system due to the solute-atoms is

$$G = N_1 H_1 + n_1 H_1{}^b - \mathrm{k}T\{\ln(n!N!) - \ln[(n - n_1)!n_1!(N - N_1)!N_1!]\} ,$$

where k is Boltzmann's constant and T is the absolute temperature. By minimising G and introducing mole fractions, this relation yields

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$$X_1{}^b = \frac{X_1 \exp(-Q/kT)}{1 - X_1 + X_1 \exp(-Q/kT)}, \quad (1)$$

where $Q = H_1{}^b - H_1$. (2)

In the above derivation only the configurational entropy was considered. Strictly, the vibrational entropy should also be taken into account. If vibrational entropy changes of the grain-boundary due to solute segregation into it are ignored, then equation 1 becomes

$$X_1{}^b = \frac{X_1 \exp(-Q/kT) \exp(\Delta S/k)}{1 - X_1 + X_1 \exp(-Q/kT) \exp(\Delta S/k)}, \quad (3)$$

where $\Delta S = S_1{}^b - S_1$ (the difference between the excess entropy of solute in the grain-boundary and in the perfect lattice). If, however, solute segregation to a low-angle grain-boundary is under consideration, the problem should be treated by the method of Bauer [3] in which he evaluates the vibrational entropy change of the dislocation itself when solute-atoms adsorb onto it. It is difficult to estimate the effect of segregation on the vibrational entropy of a high-angle grain-boundary, but it is quite possible that it may be important since solute-atoms are known to "pin" grain-boundaries and inhibit their movement [4]. This effect then should influence the vibrational characteristics of the grain-boundary in a manner somewhat analogous to the case of solute segregation to dislocations.

Q in equation 1 may be interpreted as an interaction energy and it may arise from elastic, electronic, and chemical forces. If, for example, the strain energy of a solute-atom can be relieved by segregation to a region that is already distorted, it provides a large driving force for segregation. This size effect interaction is usually the most important contribution to the solute-atom/grain-boundary binding energy in metals. Theoretical calculations of the elastic interaction energy based on dislocation models of grain-boundaries were conducted by Lücke and Detert [4] and by Webb [5]. A typical intereaction energy for metals is in the order of 0.1 to 0.2 eV. An interaction due to the different electronic behaviour of solute-atoms in the interior of a crystal and in the grain-boundary will also exist; however, calculations along these lines are difficult because very little is known about the electronic nature of a grain-boundary. Lücke and Detert reasoned that since a grain-boundary has liquid-like characteristics, an overall estimate of possible grain-boundary segregation for a given alloy system could be related to the ratio of the probability of finding the solute-atom in the liquid to the probability of finding it in the solid. This ratio was assumed to be represented by the equilibrium distribution coefficient between the liquidus and the solidus near the melting point of the solvent, and could therefore be obtained directly from the phase diagram.

It is conceivable that in homopolar crystals, chemical exchange bonding between unpaired electrons will contribute significantly to the binding energy for grain-boundary segregation in a manner analogous to the hypothesis of chemical bonding at dislocations in these materials [6]. Since grain-boundaries in germanium and silicon are known to possess certain charged states [7], it is also possible that electrostatic interactions may occur. This effect will probably be small at high temperatures, however.

3. Experimental

3.1. Previous work

A great deal of experimental work has been reported on solute-atom/grain-boundary interactions. Reference is made to an extensive review of this subject by Westbrook [8] in which he discusses both the theoretical and experimental aspects of equilibrium grain-boundary segregation.

Means of investigating foreign-atom segregation at grain-boundaries may be divided into direct and indirect methods. Direct methods allow identification of the segregating element and often provide a quantitative measure of the amount and distribution of such species. Examples of this method are chemical and autoradiographic techniques. Indirect methods are limited to a qualitative assessment of the existence of segregation, and any calibration ultimately rests upon the development of a direct technique for the same system. A number of these methods are metallography, X-ray techniques, surface energy measurements, electrical properties, microhardness, and ultrasonic absorption. Details of these experimental methods are to be found in Westbrook's paper. It should be stressed that a great deal of care must be taken with most of these methods to ensure that room temperature observations are representative of equilibrium conditions at the temperature in question.

Quenching rates, for example, must be great enough to prevent grain-boundary precipitation effects.

Most of the previous studies have involved indirect experimental methods, and little direct evidence exists for enhanced grain-boundary solubility. It has been suggested that strong chemical bonding may occur between solute-atoms and grain-boundaries in homopolar crystals, so it may be expected that such an effect could result in measurable solubility differences between single-crystal and polycrystalline material. We therefore decided to measure the solubility of copper in polycrystalline silicon in conjunction with a unified study of thermodynamic interactions in covalent solutions [9]. Hall and Racette [10], in fact, have stated that the solubility of copper in polycrystalline silicon is substantially greater than in single-crystal material, but a quantitative evaluation was not conducted.

3.2. Solubility Measurements

To establish an accurate base-line, the solubility of copper in both single-crystal and polycrystalline silicon was determined. The float-zoned single-crystal silicon (2000 Ω-cm) was purchased from Texas Instruments Inc* and the high-purity polycrystalline material was vapour-grown by the Dow Corning Corporation†. A photomicrograph showing the structure of the polycrystalline silicon is given in fig. 1. Slices about 1 mm thick were cut from the commercial ingots with a diamond saw. The wafers were then lapped on 600 mesh silicon carbide paper, and cleaned with high purity acetone.

For solubility determinations above the eutectic temperature, the commonly used plate-and-anneal method was employed. Using a standard $CuSO_4$ electroplating bath, the semiconductor slices were displacement-plated with a copper film about 2 μm thick. The bath also contained a small amount of HF to reduce the oxide layer on the samples, thereby ensuring an adherent film. The plated samples were then diffusion-annealed within a quartz furnace tube which was suitably connected to provide an atmosphere of purified argon. The temperature of the electrical resistance furnace was maintained to $\pm$ 1° C. When the samples were saturated they were cooled quickly in air, by quenching on a copper block. Annealing times were calculated on the basis of achieving 99% saturation using the experimental diffusion data reported by Boltaks [11].

Figure 1 Photomicrograph of vapour-grown polycrystalline silicon perpendicular to the growth direction, CP-4 etch (× 140).

Copper concentrations were determined by neutron-activation analysis using a splat-cooled aluminium/copper alloy as a standard. Reference is made to Dorward [9] for the details of the procedures.

Solubility equilibrations below the eutectic temperature were not conducted in the manner described above, because the method yielded time-dependent metastable "solubilities". It was found that nucleation and growth in the diffusion zone of the intermediate phase, Cu_3Si, was retarded, and consequently the initial equilibration phase was essentially pure copper. Instead, the silicon was equilibrated with Cu_3Si which was prepared by melting together appropriate amounts of copper and silicon in an alumina crucible. Silicon slices and powdered Cu_3Si were sealed in evacuated quartz capsules which were then placed in the annealing furnace. Equilibration by this method occurred via the copper vapour phase. Care was taken to ensure that a possible rate limitation at the vapour-silicon interface did not influence the solubility results.

4. Results

The experimental solubility of copper in single-crystal silicon is shown as a partial phase diagram in fig. 2. A few of the "solubilities" as determined by the plate-and-anneal method of equilibration are included for comparison. From the slope of this curve below the eutectic

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temperature, the heat of solution of copper in silicon (with respect to Cu_3Si) was determined to be 40.2 ± 0.5 kcal/mole of Cu. The error is a probable error based on a computerised least squares analysis of the data.

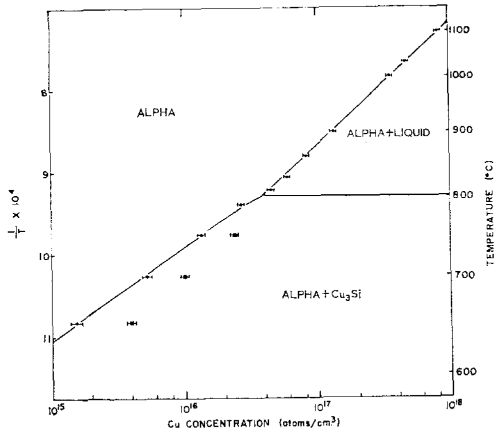

Figure 2 Solubility of copper in pure single-crystal silicon (circles). Many of the points represent duplicate determinations [9]. The squares are "solubilities" determined by the plate-and-anneal method.

The solubility of copper in polycrystalline silicon is shown in fig. 3. The dot-dashed line, obtained as a difference between these results and those of the solubility investigation in single-crystal silicon, is assumed to represent the solubility (on a bulk sample basis) of copper in the grain-boundaries. The heat of solution of copper in silicon grain-boundaries (with respect to Cu_3Si) was calculated from the slope of this plot to be 6.3 ± 0.4 kcal/mole. An assumption inherent in the above calculation is that the heat of solution is concentration-independent over the composition range considered. The interaction energy as given by equation 2 is then −33.9 ± 0.9 kcal/mole or −1.47 ± 0.04 eV/atom. Substitution of this value into equation 1 gives a grain-boundary mole fraction of $X_{Cu}{}^b = 0.43 \pm 0.10$ at 700° C where $X_{Cu} = 1 \times 10^{-7}$.

5. Discussion

It was found that the solubility of copper in polycrystalline silicon is greatly enhanced as compared to single-crystal material. The enthalpy of solution is also much less ($H^b - H = -1.47 \pm 0.04$ eV); and this difference may be regarded as the binding energy of copper-ions to grain-boundary regions. This is much larger than binding energies in metals which have been estimated to be a few tenths of an electron volt. Van Beuren [6] has suggested that strong chemical bonds may form between unpaired electrons at dislocations in homopolar crystals. It appears reasonable, therefore, that similar effects could occur at grain-boundaries, since they are probably regions of broken covalent bonds.

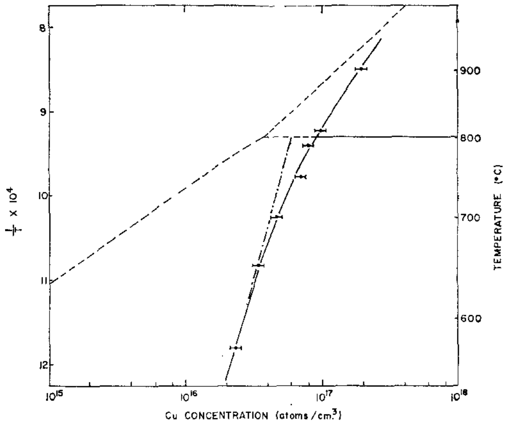

Figure 3 Solubility of copper in pure polycrystalline silicon. The dashed line represents the single-crystal results, and the dot-dashed line gives the grain-boundary solubility (on a bulk sample basis).

In calculating the binding energy it was assumed that the enthalpy of solution is independent of concentration; and the linearity of the ln X^b versus $1/T$ plot tends to support this assumption. A calculation of the grain-boundary solubility from equation 1 (a mole fraction of 0.43 ± 0.10) would seem to make this calculation suspect, since Henry's law is usually obeyed only up to a maximum concentration of about 1 or 2 at. % in normal non-ideal solutions. However, if the binding enthalpy is primarily concerned with only one nearest-neighbour bond, we expect Q to be relatively concentration-independent.

An attempt was made to estimate the grain-boundary area by metallographic studies. Fig. 1 shows that the grain structure of vapour-grown silicon is very complex and consequently a precise determination was impossible. The polycrystalline ingots have a major structure of columnar grains about 0.5 mm in diameter. These major grains contain a dense substructure which appears to be composed of twinned regions separated by low-angle grain-boundaries. The high-angle grain-boundary area contributed by the columnar grains is about 40 cm^2/cm^3. Since approximately 10^{15} $atom/cm^2$ constitute a monolayer, the maximum concentration of solute in a polycrystalline sample which can be ascribed to the high-angle grain-boundaries is about 4×10^{16} $atom/cm^3$. This value is close to the solubility limit obtained in this investigation, suggesting that the grain-boundaries are almost saturated. It is quite possible, however, that a portion of the excess copper is actually situated in the interior of the columnar grains, so the solubility in large-angle boundaries is probably less than estimated above.

Another factor which should be considered is that of thermal entropy, which was disregarded in the theoretical calculation of grain-boundary solubility. Reference to equation 3 shows that a negative entropy change lowers the solubility from that determined on the basis of enthalpy effects alone. If strong chemical bonding is involved with the segregation of solute-atoms to grain-boundaries, it could be expected that the tight binding would result in lower vibrational entropies (high frequencies), and hence tend to counteract solubility enhancement. Copper in silicon (predominantly an interstitial) has been found to have a large positive thermal entropy [12], and a major portion of this effect was ascribed to the absence of chemical bonding. If copper in grain-boundaries is tightly bound, on the other hand, a large negative thermal entropy change should accompany the transfer of an atom from an interstitial position in a single-crystal region to a grain-boundary area. Entropy changes of the grain-boundary itself may also influence the degree of grain-boundary segregation. Since solute-atoms often act as pinning points for grain-boundaries, the situation may be subject to the theory of Bauer [3] on the binding entropy of solute-atoms to dislocations. The quantitative treatment of this problem is complex, and could be even more difficult for high-angle grain-boundaries.

In summary, the grain-boundary solubility is probably less than that estimated here, but it was not possible to make a quantitative determination of the actual concentration. If, however, the grain-boundary solubility is in the order of even 1 at. %, this represents a difference of four to six orders of magnitude between the copper concentration in single-crystal and in grain-boundary regions over the temperature range 600 to 800° C. We also note that Lücke and Detert's postulate relating the degree of grain-boundary segregation to the equilibrium distribution coefficient [4] is qualitatively supported by the present work. The equilibrium distribution coefficient of copper in silicon* is much lower than is normally encountered in metallic systems (4×10^{-4} compared to 0.01 to 0.1), and therefore one could expect on this hypothetical basis that solubility enhancement at silicon grain-boundaries would be relatively high.

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*Taken as X_{Cu} (solidus)/X_{Cu} (liquidus) near the melting point of silicon.