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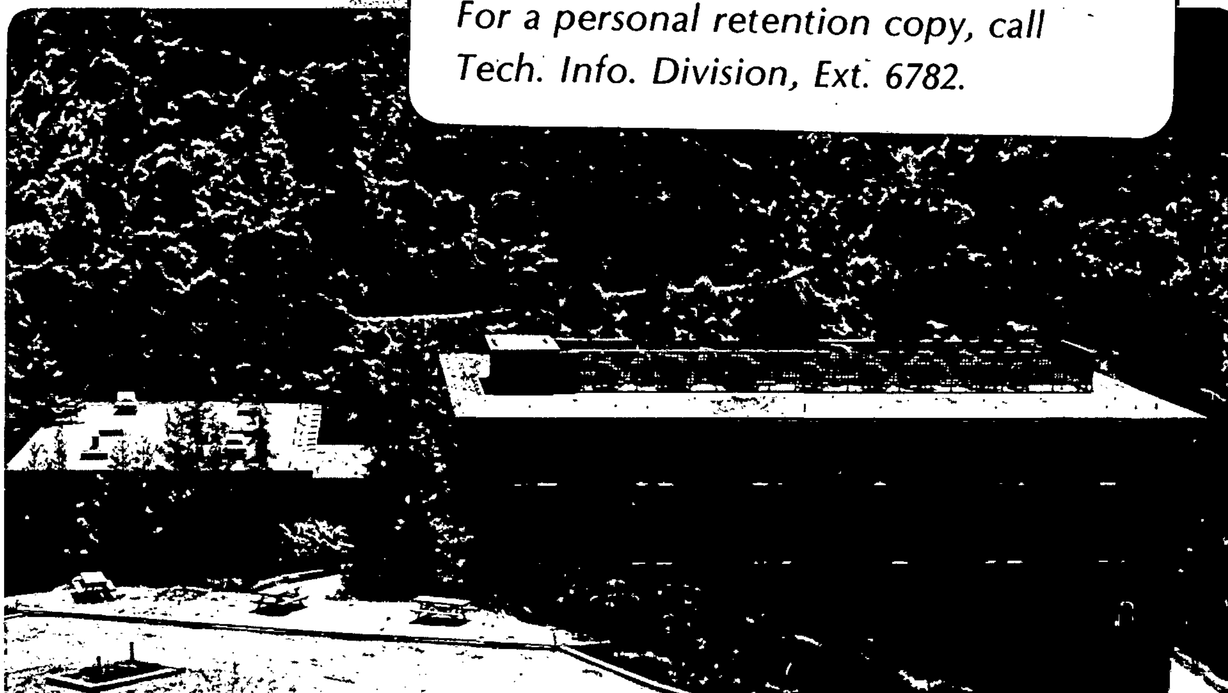

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A Scanning Transmission Electron Microscopy Microanalytical Study of Phosphorus Segregation at Grain Boundaries in Thin-Film Silicon*

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Abstract

Phosphorus segregation at grain boundaries in thin-film silicon has been investigated by scanning transmission electron microscope (STEM) x-ray micro-analysis. Low-pressure chemically vapor-deposited silicon was heavily diffusion doped and subsequently annealed at 650, 700, 750 or 800°C. Enhanced phosphorus concentrations were observed at grain boundaries with increasing levels at lower annealing temperatures. The amount of segregation was also found to vary from boundary to boundary in each specimen. The average energy of segregation was evaluated as 7.5 kcal/mol..

The grain boundaries in fine-grained polycrystalline silicon have been observed to greatly affect resistivity and mobility at low to moderate dopant levels [1-3]. In general, the complete description of this problem, as with all lattice defects in semiconductors, is extremely difficult; however, some simplification can be adopted. First, it should be noted that grain boundaries can induce defect states in the bandgap which may serve to capture majority carriers. Secondly, grain boundaries may exhibit segregation of the dopant, possibly electrically neutralizing these atoms. Until recently, only the former effect had been considered in any detail [2,3].

In previous studies of segregation of phosphorus and arsenic, resistivity and Hall mobility measurements were used to infer the number of dopant atoms segregated at grain boundaries [4,5]. Unfortunately this approach averages over the effect of the grain boundaries and other defects in the thin-film (e.g. ion-implantation damage).

This study directly examines phosphorus segregation at individual grain boundaries via STEM x-ray microanalysis. Work was performed with a Philips EM400 STEM equipped with a Kevex energy dispersive spectrometer. Details of this technique may be found in Ref. 6.

Silicon films were deposited at 630°C by low-pressure chemical vapor deposition to a thickness of 275nm. These were heavily doped by a 40 minute thermal treatment at 950°C in PH_3 followed by a deposition of a SiO_2 layer to limit out-diffusion during annealing. Samples were then annealed at 800, 750, 700 and 650°C to produce an approximately uniform dopant distribution through the film as determined by Auger electron spectroscopy depth profiling. The phosphorus concentration given by this method was 0.6 at%. Electron microscope samples were subsequently prepared by thinning from the backside of the wafer.

Specimens were examined in the STEM at an operating voltage of 100kV and a probe diameter of 10nm. Data were obtained by placing the probe on a grain boundary to acquire an x-ray spectrum, then sequentially moving the probe along the grain boundary (acquisition time was generally a few minutes, depending on grain boundary length and contamination rate). The STEM image was used to select a grain boundary, while the microdiffraction pattern obtainable during STEM operation was employed to make certain the probe was accurately positioned on the grain boundary. The excess phosphorus at the grain boundary was determined by comparing this spectra with one obtained by scanning the probe over a region surrounding the grain boundary (Fig. 1). In all cases, the Cliff-Lorimer method was used for quantitative analysis of the x-ray data [7]. The detection limit for phosphorus segregated at a grain boundary was empirically found to be approximately $8 \times 10^{13}/cm^2$, this being equivalent to a uniform concentration of about $10^{20}/cm^3$ in the probe (.2 at%).

Some grain boundaries in all specimens exhibited no phosphorus above the detection limits of this method while the rest had varying levels of segregated phosphorus. In Table I, the maximum and minimum levels of segregation are given for observations at each annealing temperature along with the average value for all grain boundaries. The average value increases with decreasing temperature as expected for equilibrium segregation; however, the varying level of segregation at a given temperature implies a variation in grain boundary structure. A limited amount of research on this aspect of grain boundary segregation has been performed, entirely for metals [8,9]. These studies suggest that the level of segregation increases with boundary disorder since increasing disorder implies the existence of more preferred sites for solute atoms and/or a greater free energy reduction at these sites. Geometrically-based theories of grain boundary structure

have been highly successful in the description of metallic boundaries, and recent observations indicate that such geometrical models provide a partial basis for prediction of grain boundary structure--and hence properties--in covalently-bonded materials [10-12]. Twin boundaries in the specimens studied revealed negligible segregation. This is expected due to their high degree of order. Additional work on this aspect of segregation is being performed on large-grained material.

To eliminate the possibility that precipitation in this heavily doped material might be causing anomalous results, specimens were imaged at high spatial resolution in TEM. A few objects exhibiting dislocation-loop type contrast were found in material annealed at 650 and 700°C. Assuming these arise from phosphorus atom condensation, there were too few to affect the matrix phosphorus concentration.

For a thermodynamic analysis of the data, a simple model of grain boundary segregation as outlined by McLean is applied [13]. The free energy of a solute atom is

$$G = PE + pe - kT \ln \Omega \ ,$$

$$\Omega = \ln n!\,N! - \ln (n-p)!\,p!\,(N-P)!\,P! \ ,$$

where E is the energy of a solute atom at a grain site, e is this energy at a grain boundary site, P is the number of dopant atoms at grain sites, p the number of grain boundary sites, N is the number of grain sites, n the number of grain boundary sites, and k ln is the configurational entropy of the dopant. Minimizing G gives

$$\frac{p}{n-p} = \frac{P}{N-P} \exp\left(\frac{E-e}{kT}\right)$$

or

$$C_{GB} = \frac{Ce^{Q/RT}}{1 - C + Ce^{a/RT}} ,$$

$$C_{GB} = p/n, \; C = P/N \; , \; Q\left(\frac{cal}{mol}\right) = N_A\,(E - e) \; .$$

The energy of segregation term, Q, is commonly expressed in these units; furthermore, at $C \ll 1$

$$C_{GB} = \frac{Ce^{Q/RT}}{1 + Ce^{Q/RT}} \; .$$

Here C is the concentration of dopant in the matrix and C_{GB} is the concentration of dopant at grain boundary sites. In the temperature range studied with C = 0.6%, the segregation is a non-linear function of C. To evaluate C_{GB}, $C_{GB} = 1$ is taken to correspond to $6.8 \times 10^{14}/cm^2$ (the atomic density of a (100) plane) since a saturated grain boundary contains approximately one monolayer of dopant [14]. In Fig. 2, a theoretical curve is fitted to values of $\bar{C}_{GB}$ as a function of temperature yielding an average value for the energy of segregation, $\bar{Q}$, of 7.5 kcal/mol. Similarly, the values of C_{GB}^{max} and C_{GB}^{min} respectively yield upper and lower limits on Q. This gives Q_{max} = 10 kcal/mol and $Q_{min} \leq 5$ kcal/mol. Actually, both Q and the saturation level are likely to be functions of grain boundary structure as indicated in the previous discussion.

Mandurah et al. examined phosphorus segregation in similar material via resistivity and Hall mobility measurements [5]. Their films were doped by ion-implantation and annealed to yield a uniform average concentration of .04%, about

one-tenth that of this study. The material was evaluated for annealing temperatures in the range 800 to 1000°C, which is contiguous to the range examined here. They found the heat of segregation to be 10.2 kcal/mol, suggesting a decrease in Q at lower temperatures and/or at high dopant concentrations. A second possibility is that the average grain boundary saturation level is somewhat lower than assumed here; closer to half a monolayer.

This study has directly confirmed that phosphorus segregation occurs at silicon grain boundaries in appropriately annealed specimens, and that the density of segregated dopant varies from boundary to boundary. In general, STEM microanalysis provides chemical data of high spatial resolution, but is currently limited in semiconductor applications by relatively poor solute detection limits.

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Table I

Temperature of Anneal (°C)	C_{GB}^{min}	C_{GB}^{max}	$\bar{C}_{GB}$
800	< .12	.24	.16
750	"	.46	.19
700	"	.52	.23
650	"	.57	.28

Table I. The minimum, maximum, and average observed grain boundary phosphorus concentrations for each annealing temperature. $C_{GB} = 1$ is defined to correspond to $6.8 \times 10^{14}/cm^2$. C_{GB}^{min} indicates the error inherent in all the measurements.

Fig. 1. Sample x-ray spectra (smoothed) comparing a grain boundary spectrum (——) with a normalized matrix spectrum (.....).

Fig. 2. Fit of Eq. (4) to data by selection of $\bar{Q}$, the average energy of segregation.

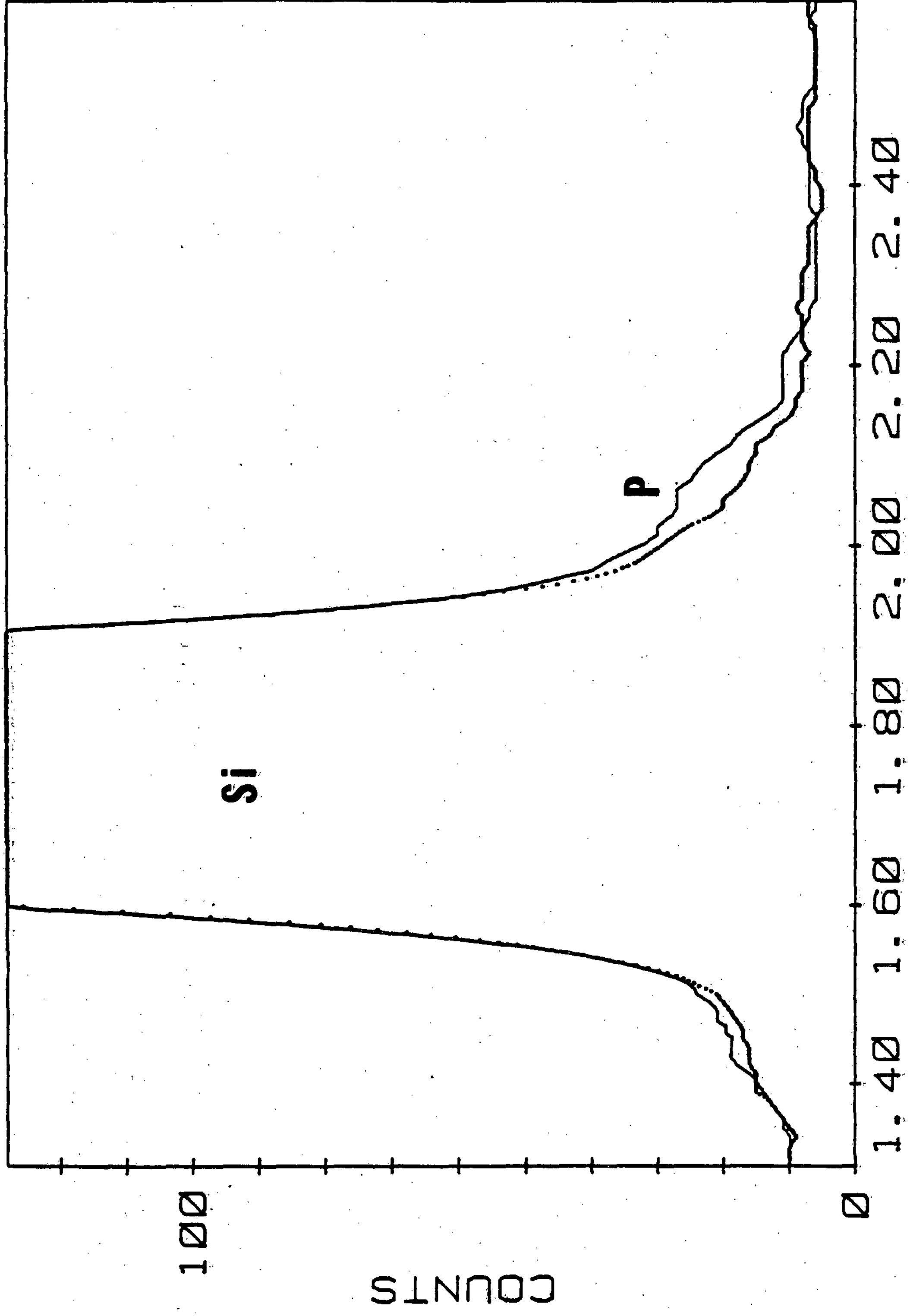

Fig. 1

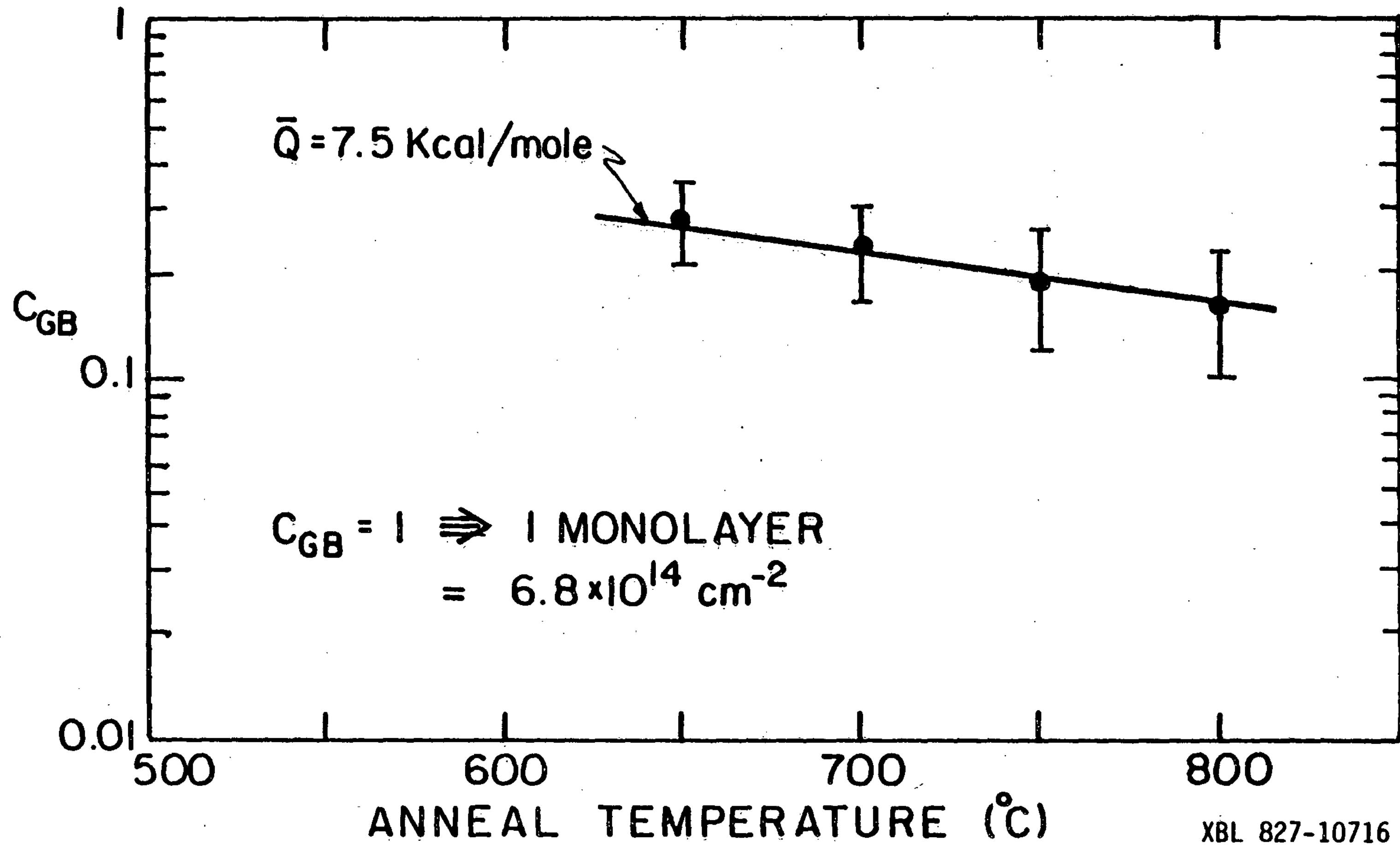

Fig. 2

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