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GRAIN BOUNDARY DIFFUSION IN POLYCRYSTALLINE SILICON FILMS ON SiO₂

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Résumé. - La différence préférentielle intergranulaire dans des couches de silicium polycristallin LPCVD recuits par laser cw sur insulateur SiO₂ a été étudiée et le coefficient de diffusion intergranulaire D' pour le phosphore déterminé. Des diodes Mesa ont été fabriquées dans des couches de silicium polycristallin à gros grains par photolithographie standard, méthodes d'attaque et implantation ionique. Le mode de courant induit (EBIC) de la MEB a permis de mesurer directement les longueurs de diffusion des dopants le long des joints de grains qui coupent la jonction p-n. Nous avons trouvé une variation de la profondeur de pénétration en $t^{1/4}$ et que la variation du coefficient de diffusion en température suivait la loi d'Arrhénius. La formulation exacte du problème de diffusion intergranulaire donnée par Whipple nous a permis d'évaluer numériquement les données expérimentales.

Abstract. - The enhanced grain boundary diffusion in cw laser processed LPCVD polycrystalline silicon films on insulating SiO₂ has been investigated and the grain boundary diffusion coefficient D' for Phosphorus has been determined. Mesa diodes were fabricated in the large grain poly-Si films by standard photolithographic and etching methods and subsequent ion implantation. The electron beam induced current mode (EBIC) of the SEM allowed direct measurement of the dopant diffusion length along the grain boundaries intersecting the p-n junction. We have found a $t^{1/4}$ dependence of the penetration depth and Arrhenius behavior for the temperature dependence of the diffusion coefficient. The numerical evaluation of the experimental data is based on Whipple's exact solution of the grain boundary diffusion problem.

1. Introduction. - Grain boundaries play an essential role in polycrystalline materials and because of the technological impact grain boundary diffusion has been an active area of research [1,2]. Current interest in polycrystalline silicon films arises from its potential use as electronic material for the fabrication of thin film transistors. Recent experiments have demonstrated large improvements in MOS device performance in polycrystalline Si whose grain size has been increased by laser processing [3,4,5,6]. In general, beam crystal-

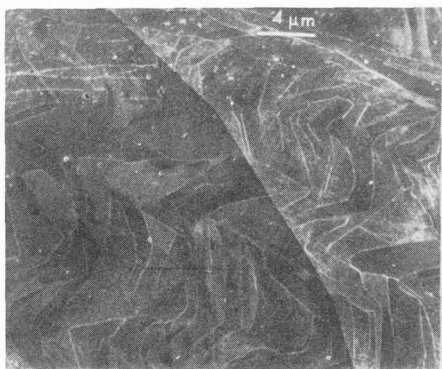


Fig.1a): SEM micrograph showing typical surface morphology of laser processed large grain polycrystalline Si on insulator

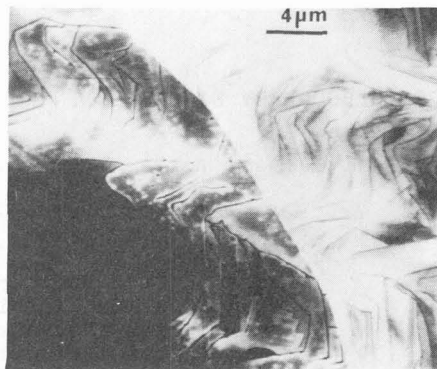


Fig.1b): corresponding EBIC image of the same sample area

lization enlarges the grain size to dimensions comparable to those of the thin film devices and hereby minimizes the detrimental effects of grain boundaries such as reduced lifetime and mobilities [7]. Very small devices, however, exhibit large leakage currents as grain boundaries form channels for rapid diffusion of source and drain dopants which act as shunt paths [6]. This paper describes the determination of the grain boundary diffusion coefficient of phosphorus in poly-Si across a p-n junction by the electron beam induced current mode (EBIC) of the SEM.

2. Experimental Procedure.— Thin polycrystalline Si films were deposited by low-pressure-chemical-vapor-deposition (LPCVD) to 0.5μm thickness on wafers covered with 1μm of steam oxide. These wafers were subsequently recrystallized by irradiation with a 10 W beam of a cw Ar⁺ laser. In the irradiated area the film is completely melted so that heterogeneous nucleation in the wake of the molten zone results in the formation of large 5- 10μm Si grains. The EBIC investigation required a p-n junction in the sample and for this purpose the wafers were uniformly implanted with a Boron ion dose of $2.5 \times 10^{12}/\text{cm}^2$ at 160 keV. The wafers were oxidized to form a 100nm thick SiO₂ layer on the Si film, which was then patterned by standard lithographic and etching methods to create an array of 120μm diameter holes. Through these holes P ions were implanted with a dose of $7 \times 10^{15}/\text{cm}^2$ at 35 keV. In this way many lateral p-n junction diodes were fabricated on a single 3" wafer. Figure 1a shows the general surface morphology of the laser processed large grain poly-Si film and 1b) the corresponding EBIC image. Prior to microscopical observation the oxide film was chemically stripped from the surface and the grain boundaries have been delineated by a 5 sec Schimmel etch [8]. The diffusion experiments were carried out in a furnace under flowing Nitrogen atmosphere. The individual samples were subjected to different tem-

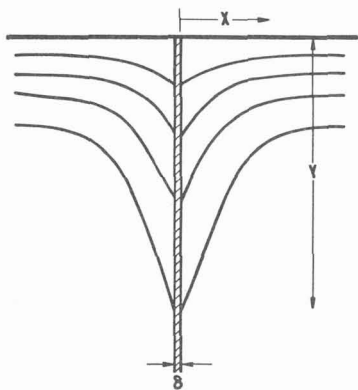


Fig.2: Schematic of isoconcentration contours caused by rapid diffusion along grain boundary slab of thickness

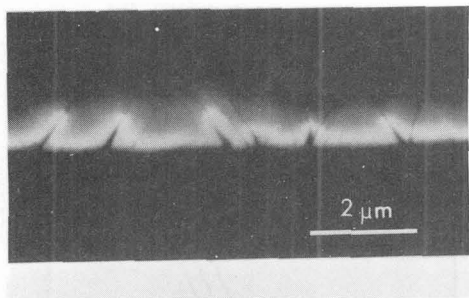


Fig.3a): Close-up of EBIC image of the p-n junction region showing grain boundary diffusion



Fig.3b): SEM secondary electron image of the same p-n junction region after Schimmel etch

perature cycles to obtain data as a function of time and temperature.

3. Grain Boundary Model.- Grain boundary diffusion experiments can seldom be decoupled from lattice diffusion because the diffusing species is always leaking into the adjoining lattice. For a given diffusion distance, y , along the boundary and at a constant temperature we expect to find isoconcentration contours with varying diffusion time as schematically depicted in Fig.2. This situation is indeed found experimentally as the EBIC micrograph in Fig.3a demonstrates. Here the p-n junction is imaged with the P doped n-type Si region in the lower half and the B doped p-type Si region in the upper half of the diode structure. The dark spikes protruding into the upper B doped region correspond to grain boundaries (see Fig.3b) and provide a direct measure for the lateral impurity penetration depth y . These dark spikes have also been detected by voltage-contrast in the SEM [9]. In order to obtain information that is extrapolable to arbitrary temperature time cycles, the coupled lattice-grain boundary diffusion problem must be analyzed. The first mathematical analysis of this problem was performed by Fisher [10], who solved the coupled lattice-grain boundary diffusion equations in an approximate fashion by assuming that the problem is analogous to the diffusion of heat along a thin copper foil imbedded in cork. The high diffusivity region in the grain boundary is represented by an isotropic slab of uniform thickness δ inside which the diffusion coefficient is D' instead of D in the adjacent bulk material. The problem is then to solve Fick's diffusion equation for the regions inside and outside the slab subject to the normal continuity conditions at its boundaries.

$$\text{Inside the slab:} \quad D' \nabla^2 C' = \frac{\partial C'}{\partial t}$$

$$\text{Outside the slab:} \quad D \nabla^2 C = \frac{\partial C}{\partial t}$$

[C and C' denote concentrations outside and inside the slab]
The boundary conditions at the edge of the slab are:

$$C = C' \quad D' \frac{\partial C'}{\partial x} = D \frac{\partial C}{\partial x}$$

In addition, some chosen conditions on the concentration at the free surface are required. In our experiment the ion implanted diodes represent an infinite diffusion source. That means the surface concentration of the diffusing species is maintained at a constant value C_0 from $t = 0$ onwards.

$$C(x, y, t) = C_0 \quad \text{at } y = 0 \text{ for } t \geq 0$$

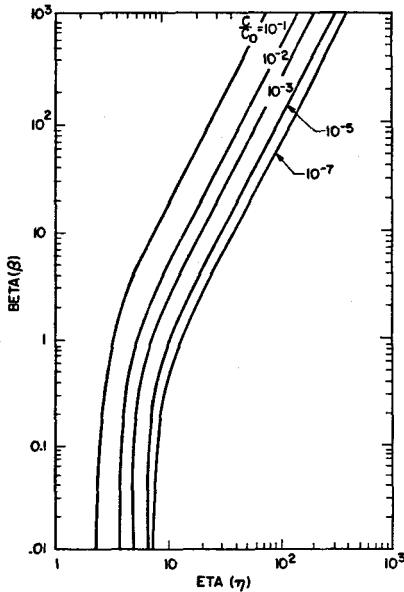


Fig.4a): Beta as a function of Eta for various relative concentrations using the exact Whipple solution (from Ref. 13)

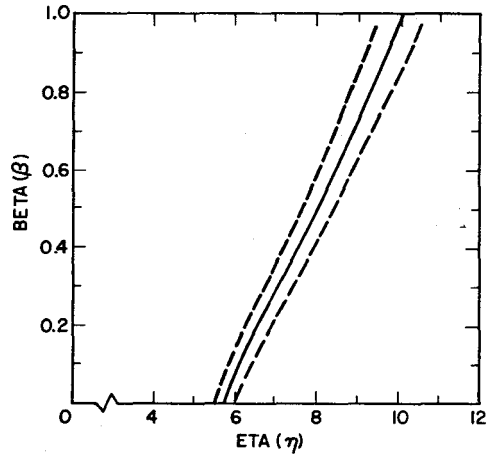


Fig.4b): Whipple's exact solution for grain boundary diffusion at $\frac{C_0}{C_\infty} = 0.00005$ (from Ref.13)

Combining the boundary conditions and expressing $C'(x,y,t)$ as a power series in x^2 the condition

$$D' \frac{\partial^2 C}{\partial y^2} + \frac{2D}{\delta} \frac{\partial C}{\partial x} = \frac{\partial C}{\partial t}$$

is obtained which has to be satisfied at the boundary.

Whipple solved this problem exactly by a method of Fourier-Laplace transforms [11]. Whipple's exact solution for $C(x,y,t)$ may be written:

$$\frac{C}{C_0} = \operatorname{erfc} \frac{\eta}{2} + \frac{\eta}{2\pi^{1/2}} \int_1^\infty \frac{d\sigma}{\sigma^{3/2}} \exp \frac{-\eta^2}{4\sigma} \operatorname{erfc} \frac{1}{2} \left[\frac{\sigma-1}{\beta} + \xi \right]$$

with the reduced and dimensionless coordinates

$$\eta = \frac{y}{(Dt)^{1/2}}; \quad \xi = \frac{x - \frac{1}{2}\delta}{(Dt)^{1/2}}$$

and a parameter

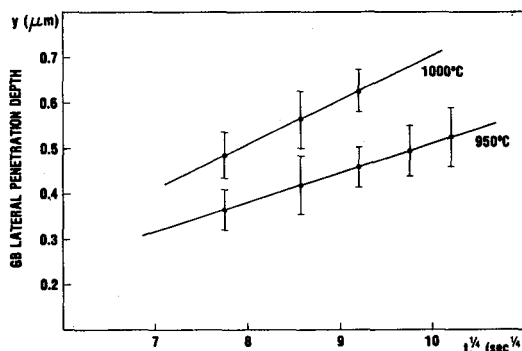
$$\beta = \frac{D'}{2D} \frac{\delta}{(Dt)^{1/2}}$$

The integral can be evaluated numerically to high precision. Because of the complexities involved in the application of the exact solution in integral form the results are usually presented in graphical form [12]. Figure 4a illustrates the behavior of Whipple's exact mathematical solution for several relative concentrations and Fig.4b presents the dependence of β on η for values of β less than one, from the work of Canon and Stark [13].

4. Results and Discussion.- In graphical form Whipple's exact solution can immediately be applied for the analysis of experimental diffusion length measurements. It is obvious that the exact solution to the grain boundary diffusion problem yields the product $D'\delta$ and D' cannot be measured directly. For our calculations we will assume δ is 5 Å

Fig.5: Phosphorus grain boundary diffusion length as a function of $t^{1/4}$ at a temperature of 950°C and 1000°C.

which is the most widely used value in the literature. In Fig.5 we have plotted the measured grain boundary penetration depth values, y , against $t^{1/4}$ and found a linear relationship. This demonstrates, that the grain boundary penetration depth at which a given concentration is to be found, varies as the quarter power of the annealing time. Thus the experimental results are in agreement with the exact solution for the coupled lattice and grain boundary diffusion equations.



Finally for our analysis we used Fig. 4b to extract the $D'\delta$ values from our measurements. This graph is a linear reproduction of the lower portion of the log-log plot in Fig.4a. It represents the dependence of β on η for a relative concentration $C/C_0 = 0.00005$, so that a penetration measurement, represented by η , determines a unique value of β which is directly related to $D'\delta$. The phosphorus concentration at the grain boundary front, where the p-n junction is formed, was equated with the boron concentration in the p-type Si region which yields the relative concentration C/C_0 . In Fig.6 the diffusion coefficients D' , obtained in this way, were plotted on a semilogarithmic scale against the inverse temperature. Figure 6 illustrates that D' exhibits Arrhenius behavior. Therefore the dependence of the grain boundary diffusion coefficient upon time is well represented by a relationship of the form:

$$D' = D_0 \exp[-Q'/kT]$$

where Q' is the activation energy for GB diffusion. The graph shows measured data points for D' in the temperature range between 900°C and 1100°C. For comparison the bulk diffusivities of phosphorus in silicon are included. D' is one to two orders of magnitude greater than the lattice diffusion coefficient D , while Q' the activation energy for GB diffusion is smaller than Q . In the early literature Queisser, Huber and Shockley reported a value of $Q' = 1.5\text{eV}$ for diffusion along low angle grain boundaries in silicon. [14]. We obtained a GB diffusion activation energy of 1.95 eV which is close to recently published data [15]. It is interesting to compare these values with the activation energy for lattice diffusion of phosphorus in

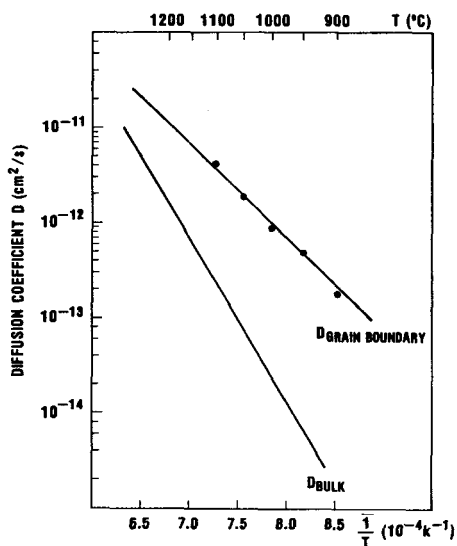


Fig.6: Grain boundary diffusivity of Phosphorus in polycrystalline Si films as a function of inverse temperature plus bulk diffusivities for comparison.

intrinsic silicon. $Q = 3.66$ eV which is roughly double the value for Q' .

In summary, we have shown that EBIC investigations are a valuable method for the determination of grain boundary coefficients of common dopants in semiconductors. The technique is far superior to earlier staining techniques for diffusion experiments. In polycrystalline Si films grain boundary diffusion clearly dominates bulk diffusion which has to be taken into account for the design of devices in such films.

5. References.-

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