Volume and dislocation diffusion of iron, chromium and cobalt in CVD $\beta$-SiC

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Abstract

Impurity tracer diffusion of $^{57}$Fe, $^{51}$Cr and $^{57}$Co in CVD $\beta$-SiC has been studied in the temperature range between 973 and 1873 K. The temperature dependence of the volume diffusion coefficients of iron and chromium can be expressed by linear Arrhenius equations. The preexponential factor and the activation energy are estimated to be $8.7 \times 10^{-15}$ m$^2$ s$^{-1}$ and 111 kJ mol$^{-1}$ for iron, respectively, and $9.5 \times 10^{-15}$ m$^2$ s$^{-1}$ and 81 kJ mol$^{-1}$ for chromium, respectively. The diffusion coefficients of iron and chromium are much higher than those of the self-diffusion in $\beta$-SiC. Furthermore, the activation energies for the diffusion of iron and chromium are about one-tenth of those for carbon and silicon in $\beta$-SiC. Therefore, it seems that an interstitial mechanism is predominant for the diffusion of iron and chromium in $\beta$-SiC. On the other hand, the diffusion coefficient of cobalt above 1673 K is higher than that of iron, while at lower temperatures it is much lower than that of iron. The difference in the diffusion coefficients at 1173 K is more than three orders of magnitude. Thus, the temperature dependence of the diffusion coefficients of cobalt shows a strongly curved Arrhenius relation. This suggests that cobalt atoms diffuse by an interstitial mechanism at higher temperatures and by a substitutional mechanism at lower temperatures. From the deeper regions of the penetration profiles of iron, chromium and cobalt the dislocation diffusion coefficients of them have been estimated. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Silicon carbide; Iron diffusion; Chromium diffusion; Cobalt diffusion; Diffusion coefficient; Activation energy; Volume diffusion; Dislocation diffusion; Interstitial mechanism; Substitutional mechanism

1. Introduction

Silicon carbide (SiC) is an important high technology ceramics in various fields of industry. It has been widely used as abrasives, grinding and cutting wheels, heat resisting materials and others, because it has great hardness and good thermal properties at high temperatures. Furthermore, SiC has high potential applicability in car engines, turbines, etc. [1]. On the other hand, the process technique of high purity or doped large-sized single crystals of SiC has been developed rapidly and its achievement has attracted much attention in semiconductor devices technology [2]. Then, information on diffusion in SiC is now required, because studies on diffusion in semiconductors have made great contributions to the semiconductor fabrication technology.

Today, the semiconductor technology requires high quality electric furnaces to process larger sized silicon wafers at higher temperatures without any contamination. Since SiC has higher strength than quartz glass at higher temperatures such as 1473 K, SiC instead of quartz glass is recently applied to the tubes and boats for the heat treatments of large sized silicon wafers. However, when the wafers are heat-treated in sintered SiC tubes and boats, metallic impurities evaporated from heating materials penetrate through the tubes and contaminate silicon wafers, which is a serious problem to be solved. The main metallic impurities analyzed are Fe, Cr, Al, Co, Ni, Cu and Na. Cu and Na result mainly from coolant and sweat, respectively. Especially, the 3d transition elements affect remarkably on the performance of semiconductor devices [3]. Recently, sintered SiC tubes and boats for the heat treatments of silicon wafers have been covered with CVD (chemical vapor deposition)-SiC coating, which is found to be very effective in preventing impurities from penetrating tubes and boats.
However, the diffusion and penetration behavior of these elements has not been known, because the reliable experimental data on diffusion in SiC have been scarcely obtained [1,4]. The reasons for this are largely due to some specific features of the material: it is often non-stoichiometric, it is very hard, it has extremely high melting temperature (peritectic reaction at 2818 K), specimens of acceptable purity and single crystals are difficult to obtain. For instance, technological SiC contains often Si or SiO₂ films at the grain boundaries. Sintering aids are also frequently used. Thus, effects of impurities, grain boundaries, pores and second phases cause many difficulties in the diffusion experiments. Because of the high melting point, high temperatures have to be used to measure any diffusion, and very high temperatures are needed to measure the volume diffusion by the conventional techniques. Furthermore, SiC appears in very many polytypes [5]. The phases most frequently found are 3C, 4H, 15R and 6H where the letters indicate the lattice symmetry (C for cubic, H for hexagonal, R for rhombohedral) and the numbers indicate the numbers of stacking layers of planes of tetrahedral in the unit cell.

As mentioned above, various conditions of SiC are unfavorable for diffusion experiments. Nevertheless, reliable diffusion data on SiC are keenly required from both academic and technological interests. So far, experiments on self-diffusion of ¹⁴C [6] and ³⁰Si [7] in the single crystal β-SiC (6H-type) made by the Lely method and of ¹⁴C [8] and ³⁰Si [9] in the polycrystal β-SiC (3C-type) made by the CVD method have been performed by Hon et al. According to them, carbon and silicon atoms diffuse by the monovacancy mechanism. On the other hand, it has been reported that stacking faults, twins and dislocations are very often observed in CVD-SiC [10,11]. Thus, the evaluation of the contributions of these lattice defects to the diffusion is also important.

The present work has been performed to reveal the diffusion behavior of the 3d-transition elements in volume and along high-diffusivity paths in CVD β-SiC. Experiments on the diffusion of iron, chromium and cobalt have been carried out with the radioactive tracers ⁵⁹Fe, ⁵¹Cr and ⁵⁷Co by a serial ion-beam sputter-microsectioning technique which enables us to measure submicron diffusion profiles at low temperatures far below the melting point of SiC.

2. Experimental

High purity polycrystalline SiC plates made by a chemical vapor deposition technique were supplied by Toshiba Ceramics Co., Ltd. The source materials of Si and C were SiH₄Clₓ and C₆H₄ₓ⁺₀.₇ which reacted on a special graphite substrate. The external view of the CVD-SiC plate was green and transparent. The mean grain size was about 300 μm. The specimen size was 10 mm square and 0.5 mm thick. One surface of the specimen was polished mirror-like. The presence of polytypes was determined by X-ray diffraction using Ni-filtered CuKα radiation. Atomic absorption spectrometry method was employed to measure the concentration of impurities in the CVD-SiC. The crystallinity and orientation of the CVD-SiC were evaluated by the X-ray diffraction method. The chemical composition of the β-SiC is given in Table 1, showing that the purity of the β-SiC is very high suitable for the diffusion experiments. The density of the β-SiC was measured to be 3.2 × 10³ kg m⁻³ which is close to 3.210 × 10³ kg m⁻³ of the single crystals of pure CVD β-SiC [12].

The radioisotope ⁵⁹Fe (γ-rays, 1.095 and 1.292 MeV; half-life, 44.6 d) was supplied in a form of ferric chloride in 0.5 kmol m⁻³ HCl solution from E.I. Du Pont de Nemours and Co. Inc., USA. The radioisotope ⁵¹Cr (γ-ray, 0.350 MeV; half-life, 27.7 d) was supplied in a form of chromic chloride in 0.5 kmol m⁻³ HCl solution from New England Nuclear Corporation, USA. The radioisotope ⁵⁷Co (γ-ray, 0.122 MeV; half-life, 270 d) was supplied in a form of cobaltous chloride in 0.1 kmol m⁻³ HCl solution from ICN Biochemical Inc., USA. A drop of the solution containing ⁵⁹Fe, ⁵¹Cr or ⁵⁷Co was put into 0.1 × 10⁻⁶ m³ of dimethyl-sulfoxide. Then some drops of the dimethyl-sulfoxide solution was dried on a flat surface of the specimen under a heating lamp. Another specimen from which the diffusion profile was analyzed after diffusion was put on the radioactive surface of the specimen and bound with a tantalum wire, and the couple of the specimens was sealed in a quartz tube at a pressure less than 2.6 × 10⁻⁴ Pa and put into an electric furnace controlled within ± 1 K, and diffusion annealing was made at temperatures in the range from 973 to 1873 K for 1.8 to 1719.6 ks.

After diffusion, the serial ion-beam sputter-microsectioning technique was employed to measure the penetration profiles of the radioisotope into the specimen. Details of the ion-beam sputter-microsectioning method were described elsewhere [13]. The Kaufman-type 3 cm ion gun supplied by Ion Tech Inc., was installed in the sputtering apparatus. The specimen was put in a stainless steel holder. A couple of the holder and the specimen was screwed to the target. The sputtered-off material was collected onto an aluminum foil. The sputtering chamber
was first prepumped to a vacuum of $5.3 \times 10^{-3}$ Pa. Pure argon gas (99.9995% purity) was introduced to the ion gun. The operating conditions of the ion beam system were as follows: beam voltage, 350 V; beam current, 7 mA; accelerating voltage, 80 V; cathode filament current, 3 A; argon gas pressure, $5.3 \times 10^{-3}$ Pa. The serial sectioning of the concentration profile of the specimen was made by sputtering, and the sputtered section was collected on the aluminum foil which was wound step by step after each sectioning like a roll film in a camera without interrupting beam current. For each specimen 20–45 successive sections were sputtered. The thickness of each section was determined from the individual sputtering time and the sputtering rate. The sputtering rate was kept constant in the range 6–10 nm min$^{-1}$ by controlling the argon gas pressure and the beam current. The latter was automatically adjusted by the power supply. In each run the sputtering rate was calculated from the total sputtering time and total decrement of the thickness of the specimen which was measured with the help of an interferometric microscope by analyzing the step in an interference pattern which occurred between protected and sputtered parts of the surface. The intensity of γ-rays from each section collected on the aluminum foil was measured by a well-type TI-activated NaI scintillation detector in conjunction with a 1024-channels pulse height analyzer.

3. Results and discussions

For one-dimensional volume diffusion of a tracer from an infinitesimally thin surface layer into a sufficiently long rod, the solution of Fick’s second law [14] is given by

$$I(X,t) \propto C(X,t) = (M/\sqrt{4\pi D_v t}) \exp(-X^2/4D_v t),$$

where $I(X,t)$ and $C(X,t)$ are the intensity of the radioactivity and the concentration, respectively, of the tracer at a distance $X$ from the original surface after a diffusion time $t$. $D_v$ is the volume diffusion coefficient of the tracer and $M$ is the total amount of tracer deposited on the surface before the diffusion.

The tracer diffusion along the high-diffusivity paths (grain boundary, stacking fault and dislocation) is the dominating mass transport process at low temperatures. Since the mean grain size of the specimen was 300 μm and furthermore the diffusion profile was measured by the sputter-microsectioning technique in the depth of submicrons, the contribution of the grain boundary diffusion to the profile is expected to be negligible. Moreover, the diffusion along stacking faults and dislocations cannot be analyzed separately, thus both the contributions are collectively analyzed by a dislocation model [15]. The solution of Fick’s law does not yield the diffusion coefficient in the dislocation $D_d$ separately, but only the product, $D_d a^2 s$, where $a$ is the effective radius of the dislocation ‘pipe’ and $s$ is the impurity segregation factor. Under the conditions of the type B kinetics [16], that is, $a < \sqrt{D_v t} < R$ (2R: average distance of dislocations), $D_d a^2 s$ is given by [17]

$$D_d a^2 s = D_v \left[ \frac{A(a)}{\partial \ln C/\partial X} \right]^2.$$

Diffusion with the type B kinetics takes place simultaneously from the surface into the bulk and down and out of dislocations into the surrounding lattice. When the diffusion length $\sqrt{D_v t}$ is sufficiently smaller than $R$, the lateral diffusion zones surrounding the dislocations are not influenced by the neighboring dislocations. The penetration profile in a serial sectioning experiment then consists of a nearly Gaussian portion in the near surface region and a dislocation tail portion in the deeper region. The slope of the Gaussian portion is associated with the volume diffusion. $A(\alpha)$ is a slowly varying function of $\alpha (= a/\sqrt{D_v t})$ and is of the order of unity [17]. $C$ is the mean concentration of tracer at the depth $X$ parallel to the surface of the specimen. Eq. (2) implies that $\partial \ln C/\partial X$ is practically independent of diffusion time as long as the conditions of the type B kinetics are fulfilled. Therefore, if an equal value of $\partial \ln C/\partial X$ is obtained for different diffusion times, the deeper region can be attributed to the dislocation pipe diffusion. If the tail slope in the deeper region is caused by the grain boundary diffusion, $\partial \ln C/\partial X$ to linear and it depends on diffusion time [17,18].

Figs. 1–3 show the typical plots of $\ln I(X,t)$ versus $X^2$ for

![Fig. 1. Examples of penetration profiles for diffusion of $^{57}$Fe in β-SiC.](image-url)
the diffusion of $^{56}$Fe, $^{51}$Cr and $^{57}$Co in β-SiC, respectively. The linearity observed in Figs. 1–3 proves that Eq. (1) holds, and thus it can be said that the volume diffusion has been concerned. When the deviation from the Gaussian behavior of Eq. (1) is observed very near the surface, it may be caused by oxidation of surface layers, which act as barriers against diffusion, or by difficulties in dissolving the radioisotopes from the form of chlorides [19]. In the present experiments, such deviation has not been observed, although in some profiles the evaporation of the radioisotopes from the surface is observed. Tails observed in all the profiles in Figs. 1–3 are due to the contribution of dislocation diffusion, as described later. The volume diffusion coefficients of iron, chromium and cobalt in β-SiC calculated from the linear slope in Figs. 1–3 are listed in Table 2, and the Arrhenius plots of them are shown in Fig. 4. The plots of the diffusion coefficients of iron and chromium show linear relationships. The temperature dependence of them is expressed by

$$D_i(\text{Fe}) = 8.7 \times 10^{-15} \exp(-111 \text{ kJ mol}^{-1}/RT) \text{ m}^2 \text{ s}^{-1} \quad (3)$$

$$D_i(\text{Cr}) = 9.5 \times 10^{-15} \exp(-81 \text{ kJ mol}^{-1}/RT) \text{ m}^2 \text{ s}^{-1} \quad (4)$$

The temperature dependence of the self-diffusion coefficients of carbon [8] and silicon [9] in β-SiC with their

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**Table 2**

| Element | $T$ (K) | $t$ (ks) | $D_i$ (m$^2$s$^{-1}$) | $\sqrt{D_i}$ (m) |
|---------|---------|---------|----------------------|------------------|
| Fe      | 1773    | 3.6     | $5.8 \times 10^{-18}$ | $1.4 \times 10^{-7}$ |
|         | 1673    | 1.8     | $2.9 \times 10^{-14}$ | $7.2 \times 10^{-8}$ |
|         | 1573    | 3.6     | $2.1 \times 10^{-14}$ | $8.6 \times 10^{-8}$ |
|         | 1473    | 3.6     | $7.8 \times 10^{-19}$ | $5.3 \times 10^{-8}$ |
|         | 1373    | 50.4    | $4.8 \times 10^{-19}$ | $1.6 \times 10^{-7}$ |
|         | 1273    | 25.2    | $2.7 \times 10^{-19}$ | $8.3 \times 10^{-8}$ |
|         | 1273    | 64.8    | $2.1 \times 10^{-19}$ | $1.1 \times 10^{-7}$ |
|         | 1173    | 57.06   | $6.9 \times 10^{-20}$ | $6.3 \times 10^{-8}$ |
|         | 1073    | 159.12  | $2.6 \times 10^{-20}$ | $6.5 \times 10^{-8}$ |
|         | 973     | 426     | $1.4 \times 10^{-20}$ | $7.7 \times 10^{-8}$ |
| Co      | 1873    | 3.0     | $1.7 \times 10^{-17}$ | $2.2 \times 10^{-7}$ |
|         | 1773    | 3.6     | $9.0 \times 10^{-18}$ | $1.8 \times 10^{-7}$ |
|         | 1673    | 3.6     | $3.7 \times 10^{-18}$ | $1.2 \times 10^{-7}$ |
|         | 1573    | 3.6     | $9.2 \times 10^{-19}$ | $5.7 \times 10^{-8}$ |
|         | 1473    | 10.8    | $2.6 \times 10^{-19}$ | $5.3 \times 10^{-8}$ |
|         | 1373    | 54.6    | $4.7 \times 10^{-20}$ | $5.1 \times 10^{-8}$ |
|         | 1273    | 322.3   | $3.3 \times 10^{-21}$ | $3.3 \times 10^{-8}$ |
|         | 1223    | 581.7   | $5.3 \times 10^{-22}$ | $1.8 \times 10^{-8}$ |
|         | 1173    | 1719.6  | $4.7 \times 10^{-23}$ | $9.0 \times 10^{-9}$ |
|         | 1173    | 1719.6  | $5.2 \times 10^{-23}$ | $9.4 \times 10^{-9}$ |
| Cr      | 1573    | 1.8     | $2.3 \times 10^{-10}$ | $6.4 \times 10^{-8}$ |
|         | 1473    | 1.8     | $1.1 \times 10^{-10}$ | $4.4 \times 10^{-8}$ |
|         | 1373    | 1.8     | $8.0 \times 10^{-10}$ | $3.8 \times 10^{-8}$ |
|         | 1273    | 1.8     | $3.5 \times 10^{-10}$ | $2.5 \times 10^{-8}$ |
|         | 1173    | 2.7     | $2.1 \times 10^{-10}$ | $2.4 \times 10^{-8}$ |
measured ranges is also shown in Fig. 4. The Arrhenius lines for both carbon [8] and silicon [9] show linearity. The preexponential factor and the activation energy for the self-diffusion have been obtained to be $2.6 \times 10^4 \text{ m}^2 \text{s}^{-1}$ and 839 kJ mol$^{-1}$ for carbon [8] and $8.4 \times 10^4 \text{ m}^2 \text{s}^{-1}$ and 911 kJ mol$^{-1}$ for silicon [9], respectively. As seen in Fig. 4, below 1873 K the volume diffusion coefficients of iron, chromium and cobalt are much higher than those of self-diffusion, however, above 2000 K all the diffusion coefficients of iron, chromium, cobalt, carbon and silicon are almost of the same order in magnitude.

The activation energies for the diffusion of iron and chromium are only about one-tenth of those for the self-diffusion. Therefore, it seems that an interstitial mechanism is operating for the diffusion of iron and chromium in β-SiC, although the solubility and the stable lattice site of the 3d transition atoms in the β-SiC have not been known.

On the contrary, the Arrhenius plot of the diffusion coefficients of cobalt shows non-linear behavior. The diffusion coefficient of cobalt in β-SiC decreases remarkably with decreasing temperature. This type of the curved Arrhenius plot has been often observed for the diffusion of hydrogen in steels owing to the trapping effect of hydrogen with lattice defects [20,21]. If the curved Arrhenius plot is also due to a trapping effect on the diffusion of cobalt in β-SiC, it is not unreasonable that the effect will be found in the diffusion of iron and chromium. However, the Arrhenius plots of the diffusion of iron and chromium show linearity, as shown in Fig. 4. Therefore, the anomalous behavior of cobalt should be attributed to other reasons. To confirm the diffusion behavior of cobalt at lower temperatures, additional experiments were performed using two other types of specimens with different density of defects; one is gray and opaque and the other is brown and transparent. Both the types of β-SiC were made with different conditions of the CVD technique. Specimen size is the same as that used in the present experiments, but the grain size of both the types is about 10 μm in contrast to 300 μm of the green and transparent β-SiC. The penetration profiles for diffusion of cobalt at 1273 and 1373 K are shown in Fig. 5. From the linear slope near the surface the diffusion coefficients are calculated and plotted in Fig. 6. The values of the diffusion coefficients of cobalt in the gray and opaque β-SiC and in the brown and transparent β-SiC are in agreement with the values for the green and transparent β-SiC at 1273 and 1373 K, although the magnitudes of the diffusion coefficients are in the order of the green and transparent β-SiC, the gray and opaque β-SiC and the brown and transparent β-SiC. These three types of the polycrystal β-SiC have grown upwards on a graphite substrate. The schematic views of cross section of the specimens are shown in Fig. 6. The V-shape large grains have grown in the green and transparent β-SiC, while the parallel fine grains have grown in the brown and transparent β-SiC. In the gray and
opaque β-SiC the V-shape but fine grains have grown. The different growth patterns of the β-SiC result in different grain size and different density of stacking faults and dislocations. However, the values of the volume diffusion coefficients are in agreement with each other, and they fit on one Arrhenius line. Therefore, the curved Arrhenius behavior of cobalt diffusion is not due to a trapping effect, which is concerned with lattice defects.

The activation energies for cobalt calculated temporarily from the diffusion coefficients at high temperatures, 1773 and 1873 K, and from those at low temperatures, 1223 and 1173 K, are 169 and 567 kJ mol⁻¹, respectively. The activation energy for the high temperature region is near the values for iron and chromium. Then the diffusion of cobalt in the higher temperature region occurs predominantly by an interstitial mechanism, however, in the lower temperature region the mechanism changes gradually to a different one. It is probably a substitutional mechanism, because the activation energy is about three times larger than that in the higher temperature region and it is about one half of the value for the self-diffusion. The diffusion behavior of 3d transition elements in silicon gives us some suggestions on the anomalous diffusion of cobalt as described below.

A considerable progress in the understanding of the properties of the 3d transition elements in silicon has been achieved [3,22,23]. It is important that the 3d transition impurities can occupy both substitutional and interstitial sites in silicon. However, they are divided into two categories according to the lattice site occupied by the 3d transition atoms. The 3d transition atoms from titanium to iron predominantly or solely occupy interstitial sites. The diffusivities from titanium to iron apparently depend on the electronic structure of atoms; the larger the atomic number, the larger the diffusion coefficient [3,23]. These atoms diffuse by an interstitial mechanism. On the other hand, cobalt and nickel atoms predominantly occupy interstitial sites, but only the minor species occupy substitutional sites [23]. Furthermore, only nickel has been reported to diffuse via the dissociative mechanism [24]. Cobalt is probably in the category of nickel [25]. In this way, the diffusion mechanism of nickel and cobalt in silicon is not the simple interstitial one. Similar diffusion behavior of 3d transition atoms in β-SiC is expected, because silicon and silicon carbide belong to covalent bond crystals. Taking account of the large activation energy for cobalt in the lower temperature region, it can be concluded that a substitutional mechanism operates predominantly for the diffusion of cobalt in β-SiC.

The typical plots of ln (I(t)/X) versus X for the diffusion of ⁵⁹Fe, ⁵¹Cr and ⁷⁷Co in β-SiC are shown in Fig. 7–9, respectively. The general features of these curves are in agreement with the type B kinetics behavior expected: almost Gaussian portions of the penetration curves in the surface-near region and a log-linear tail. The deeper region is not due to a
predominance of grain boundary diffusion but that of dislocation diffusion, because the tracers $^{59}$Fe, $^{51}$Cr and $^{57}$Co diffuse only about 0.2 μm by volume diffusion in spite of large grains of 300 μm and the penetrations are subsequently affected by high diffusivity paths. As shown in Fig. 5, similar penetration profiles are obtained for specimens with the small grain size of 10 mm; short Gaussian portion of submicrons and subsequent a long tail. Therefore, it is appropriate to deduce that a log-linear tail is due to the contribution of dislocation diffusion.

Applying Eq. (2) to the diffusion profiles in Figs. 7–9, values of the product $D_0a^2s$ are determined and are listed in Table 3. The Arrhenius plots of the dislocation diffusivities $D_0a^2s$ are shown in Fig. 10. The temperature dependence of the linear Arrhenius relations in Fig. 10 can be represented as follows:

$$D_0a^2s(\text{Fe}) = 8.0 \times 10^{-30} \exp(-73 \text{ kJ mol}^{-1}/RT) \text{ m}^4 \text{ s}^{-1},$$  \hspace{1cm} (5)

$$D_0a^2s(\text{Cr}) = 6 \times 10^{-31} \exp(-47 \text{ kJ mol}^{-1}/RT) \text{ m}^4 \text{ s}^{-1},$$  \hspace{1cm} (6)

$$D_0a^2s(\text{Co}) = 2.6 \times 10^{-22} \exp(-309 \text{ kJ mol}^{-1}/RT) \text{ m}^4 \text{ s}^{-1}.$$  \hspace{1cm} (7)

The ratio of the activation energy for dislocation diffusion (Eq. (5)–(7)) to that for volume diffusion (Eqs. (3) and (4)) is estimated to be 0.66 for iron and 0.58 for chromium. The ratio for cobalt in the lower temperature region is about 0.54. Therefore, the dislocation pipe in β-SiC provides a high diffusivity path for iron, chromium and cobalt atoms, although these atoms diffuse in the bulk β-SiC by an interstitial mechanism.

**Table 3**

Dislocation diffusivities of iron, chromium and cobalt in β-SiC

| Element | $T$ (K) | $t$ (ks) | $D_0a^2s$ (m$^4$ s$^{-1}$) | $A(a)$ |
|---------|--------|---------|-------------------------|-------|
| Fe      | 1573   | 3.6     | $3.5 \times 10^{-32}$   | 0.73  |
|         | 1473   | 3.6     | $1.2 \times 10^{-32}$   | 0.65  |
|         | 1373   | 50.4    | $2.2 \times 10^{-32}$   | 0.60  |
|         | 1273   | 64.8    | $8.3 \times 10^{-33}$   | 0.60  |
|         | 1173   | 159.12  | $2.1 \times 10^{-33}$   | 0.62  |
| Co      | 1673   | 3.6     | $8.2 \times 10^{-32}$   | 0.60  |
|         | 1573   | 3.6     | $7.1 \times 10^{-33}$   | 0.62  |
|         | 1473   | 10.8    | $1.2 \times 10^{-33}$   | 0.65  |
|         | 1373   | 54.6    | $3.1 \times 10^{-33}$   | 0.65  |
|         | 1273   | 322.2   | $2.0 \times 10^{-35}$   | 0.69  |
|         | 1223   | 581.7   | $2.3 \times 10^{-35}$   | 0.70  |
|         | 1173   | 1719.6  | $3.3 \times 10^{-36}$   | 0.73  |
|         | 1173   | 1719.6  | $2.9 \times 10^{-36}$   | 0.73  |
| Cr      | 1473   | 1.8     | $1.2 \times 10^{-32}$   | 0.67  |
|         | 1273   | 1.8     | $7.3 \times 10^{-33}$   | 0.72  |
|         | 1173   | 2.7     | $4.4 \times 10^{-33}$   | 0.73  |
Fig. 10. Arrhenius plots of dislocation diffusivities of iron, chromium and cobalt in β-SiC.

4. Conclusions

The present experimental results are summarized as follows:

1. Iron and chromium atoms in CVD β-SiC diffuse predominantly by an interstitial mechanism.
2. The temperature dependence of the diffusion coefficients of cobalt in CVD β-SiC shows a strongly curved Arrhenius line. It seems that cobalt atoms diffuse by an interstitial mechanism at higher temperatures and by a substitutional mechanism at lower temperatures.
3. From the deeper profiles the dislocation diffusivities of iron, chromium and cobalt in CVD β-SiC have been determined. Their activation energies are about 0.6—0.7 of those for the volume diffusion.

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References

[1] Hj. Matzke, Diffusion in carbides and nitrides, in: A.L. Laskar, J.L. Bocquet, G. Brevet, C. Monty (Eds.), Diffusion in Materials, Kluwer Academic Publishers, Dordrecht, Netherlands, 1990, pp. 429—455.
[2] J. Takahashi, M. Kanaya, Y. Fujiwara, Sublimation growth of SiC single crystalline ingots on faces perpendicular to the (0001) basal plane, J. Cryst. Growth 135 (1994) 61—70.
[3] K. Graff, Metal Impurities in Silicon-Device Fabrication, 2nd rev. ed., Springer, Berlin, 1999, p. 5.
[4] Hj. Matzke, Diffusion in carbides and nitrides: unsolved problems, Defects Diffusion Forum 83 (1992) 111—130.
[5] K. Järendahl, R.F. Davis, Materials properties and characterization of SiC, in: Y.S. Park (Ed.), SiC Materials and Devices, Academic Press, San Diego, USA, 1998, pp. 1—18.
[6] M.H. Hon, R.F. Davis, Self-diffusion of carbon-14 in high-purity and n-doped α-SiC single crystals, J. Am. Ceram. Soc. 63 (1980) 546—552.
[7] M.H. Hon, R.F. Davis, D.E. Newbury, Self-diffusion of silicon-30 in α-SiC single crystals, J. Mater. Sci. 16 (1981) 2485—2494.
[8] M.H. Hon, R.F. Davis, D.E. Newbury, Self-diffusion of Si in polycrystalline β-SiC, J. Mater. Sci. 15 (1980) 2073—2080.
[9] M.H. Hon, R.F. Davis, Self-diffusion of C in polycrystalline β-SiC, J. Mater. Sci. 14 (1979) 2411—2421.
[10] K. Hiraga, Application of high-resolution electron microscopy to the study of structure defects and grain boundaries in Si3N4 and SiC — a brief review, Sci. Rep. Res. Inst. Tohoku Univ. A 32 (1984) 1—20.
[11] C.H. Chu, Y.M. Lu, M.H. Hon, Growth characteristics of β-SiC by chemical vapor deposition, J. Mater. Sci. 27 (1992) 3883—3888.
[12] A.H.G. Demesquite, Refinement of the crystal structure of SiC type 6H, Acta Crystallogr. 23 (1967) 610—617.
[13] Y. Iijima, K. Yamada, H. Katoh, J.K. Kim, K. Hirano, Diffusion in iron-base amorphous alloys studied by ion-beam sputter-microsectioning technique, in: T. Takagi (Ed.), Proceedings of 13th Symposium on Ion Sources and Ion-assisted Techniques, Ionics, Tokyo 1990, The Ion Engineering Society of Japan, 1990, pp. 179—182.
[14] P. Shewmon, Diffusion in Solids, The Minerals, Metals and Materials Society, Warrendale, PA, 1989, p. 14.
[15] R. Smoluchowski, Theory of grain boundary diffusion, Phys. Rev. 87 (1952) 482—487.
[16] L.G. Harrison, Influence of dislocations on diffusion kinetics in solids with particular reference to alkali halides, Trans. Faraday Soc. 57 (1961) 1191—1199.
[17] A.D. Le Claire, A. Rabinovitch, The mathematical analysis of diffusion in dislocations, in: G.E. Murch, A.S. Nowick (Eds.), Diffusion in Crystaline Solids, Academic Press, Orlando, FL, 1984, pp. 298—318.
[18] A.D. Le Claire, The analysis of grain boundary diffusion measurements, Brit. J. Appl. Phys. 14 (1963) 351—356.
[19] S.I. Rothman, The measurement of tracer diffusion coefficients in solids, in: G.E. Murch, A.S. Nowick (Eds.), Diffusion in Crystaline Solids, Academic Press, Orlando, FL, 1984, pp. 1—61.
[20] J.P. Hirth, Effects of hydrogen on the properties of iron and steel, Met. Trans. 11A (1980) 861—890.
[21] H.H. Johnson, Hydrogen in iron, Met. Trans. 19A (1988) 2371—2387.
[22] W. Frank, U. Göele, H. Mehrer, A. Seeger, Diffusion in silicon and germanium, in: G.E. Murch, A.S. Nowick (Eds.), Diffusion in Crystaline Solids, Academic Press, Orlando, FL, 1984, pp. 63—142.
[23] H. Kitagawa, Diffusion and electrical properties of 3d transition-metal impurities in silicon, in: R.P. Agarwala (Ed.), Special Defects in Semiconductor Materials, Sciete Publications, Uetikon-Zuerich, Switzerland, 2000, pp. 51—72.
[24] H. Kitagawa, K. Hashimoto, M. Yoshida, Point defects in silicon studied by nickel diffusion, Phys. B 116 (1983) 323—327.
[25] J. Utzig, D. Gilles, Diffusion of cobalt in silicon, Mater. Sci. Forum 38/41 (1989) 729—733.