Amorphization in Silicon by Electron Irradiation

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We have found that amorphization is induced in crystalline silicon under MeV electron irradiation at low temperatures of about 25 K. The amorphization process has been observed at 25 K by means of *in situ* transmission electron microscopy and diffraction. The dose of 2 MeV electrons needed for amorphization is smaller than 7.5×10^{22} cm^{-2} at 25 K, which corresponds to 5.0 displacements per atom. The threshold electron energy for amorphization at 25 K is about 1 MeV. We discuss the mechanism of amorphization in Si based on the experimental finding.

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Amorphous silicon (a-Si) can be created from crystalline silicon (c-Si) by various processes [1–4] in addition to ordinary deposition techniques such as chemical vapor deposition. The structural transformation has attracted great attention [5,6], since Si is the most important and extensively studied semiconducting material. This Letter reports a new route of amorphization in Si: We have found that c-Si transforms to a-Si promptly under irradiation of MeV electrons at low temperatures of about 25 K, contrary to the ordinary remark that c-Si cannot be rendered into a-Si by electron irradiation. A MeV electron beam can be focused on an area smaller than 0.2 μm in diameter, can be scanned, and can penetrate about 0.5 μm into c-Si, so our finding will be applied to fabricating artificial photonic crystals and quantum dots of the two Si structures with different dielectric and electronic transport properties, for instance. In addition, our experimental results yield a more comprehensive view about the amorphization by irradiation of charged particles in Si, since the mechanism has long been studied of the amorphization by ion implantation in Si and has yet remained controversial [1,6–9]. Our finding may also be important in the field of low-energy beam processing of Si, since the maximum recoil energy of a Si atom is of the order of 10^2 eV under MeV electron irradiation.

Two kinds of thin Si specimens were made of a P-doped Czochralski Si {110} wafer: one thinned in the solution of HNO_3 and HF and the other prepared by cleavage. The surfaces of the cleaved specimens were flat and covered with less surface oxide and impurity. The specimens were set on a cooling specimen container for electron irradiation in a newly installed high voltage transmission electron microscope (TEM) of the ultrahigh voltage electron microscope center of Osaka University. The maximum thickness of irradiated areas was roughly estimated to be 0.75 μm. The electron energy for irradiation E were 1.0, 1.5, and 2 MeV. The direction of an incident electron beam was set parallel to the $\langle 110 \rangle$ zone axis. The irradiation temperature T ranged from 25 ± 5 K to 297 K. For irradiation, an electron beam was focused on a specimen of about 1 μm in diameter in this study. The focused beam had a Gaussian-like intensity profile on a specimen, so the central part of an irradiated area always received a higher flux than the average one. Using a Faraday cage, we measured the flux ϕ of the central area of a beam on a specimen position, 300 nm in diameter. The fluxes in 1, 1.5, and 2 MeV irradiations were estimated to be $(1.8–2.6) \times 10^{20}$, 2.5×10^{20}, and $(0.84–8.1) \times 10^{20}$ cm^{-2} s^{-1}, respectively. The irradiation effects were observed by means of *in situ* TEM and recorded in photographic films with a smaller flux, roughly estimated to be 10^{17} cm^{-2} s^{-1}. We found no apparent difference about the amorphization between two kinds of specimens, confirming that the amorphization by recoil implantation [10] was safely excluded. After irradiation, the specimens were examined in detail at 293 K and annealed at elevated temperatures in 200 keV TEMs. Supplemental irradiation of 0.2 and 0.3 MeV electrons was carried out at about 15 K using a 200 keV TEM and at 4.2 K using a 300 keV TEM, respectively.

During electron (2 MeV) irradiation at 25 K, we noticed that fragmented white contrast came out in bright-field TEM images [Fig. 1(a)]. Accordingly, the halo rings appeared in electron diffraction patterns, and their intensities increased with the increase of irradiation time. After the irradiation for 900 s, the central area of approximately 300 nm in diameter cleared up in the TEM image, and was fully amorphized as confirmed later on. The area received the dose of 7.5×10^{22} cm^{-2}. Assuming the threshold energy of atomic displacements in c-Si to be 14 eV, we find that the amorphization was completed after the irradiation of 5.0 displacements per atom (dpa). The irradiation introduced numerous small defects of a few nm in diameter at the periphery of the irradiation spot where the dose is lower. For comparison, another area of the same specimen was irradiated at 293 K with the same electron energy and the same flux until this area received the dose over 13 dpa. As seen in Fig. 1(b), the nucleation of numerous {113} defects was observed. Nevertheless, the crystallinity was retained at 293 K.

An amorphized area was examined at 293 K using a 200 keV TEM (Fig. 2). We confirmed that the central area was fully amorphized: In the radial distribution function which was derived from diffraction patterns of the fully

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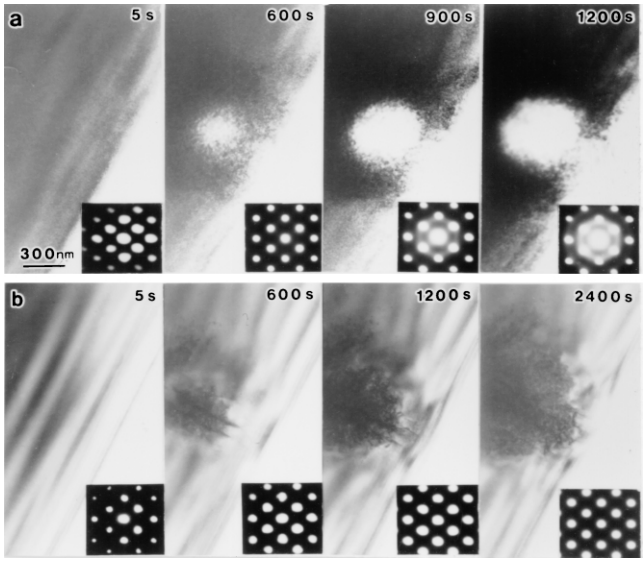

FIG. 1. (a) Amorphization process in Si observed by *in situ* TEM at 25 K. (b) Crystallinity is retained at 293 K. The irradiation time is shown in each image. The insets are the corresponding electron diffraction patterns. ($E = 2$ MeV, $T = 25$ K, $\phi = 8.35 \times 10^{19}$ cm^{-2} s^{-1}.)

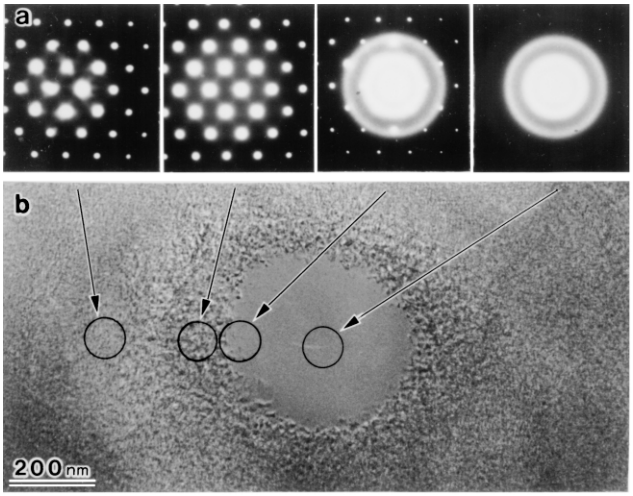

FIG. 2. Postirradiation TEM observation of the amorphized area. Electron diffraction patterns in (a) were taken from the corresponding circled areas in the bright-field TEM image in (b). A number of defects are also observed. ($E = 2$ MeV, $T = 25$ K, $\phi = 1.0 \times 10^{20}$ cm^{-2} s^{-1}, $D = 8.4 \times 10^{22}$ cm^{-2} = 5.6 dpa.)

amorphized area, the peaks locate at 0.23, 0.38, 0.57, and 0.75 nm. The third peak of c-Si at 0.45 nm is missing [11] as in a-Si produced by the other methods [12].

Because of the Gaussian-like intensity profile of a focused electron beam, the dose dependence of the structural change can be seen from the center to the periphery of an electron irradiation spot [Fig. 2(b)]. The crystal-amorphous (c-a) interface is not atomistically sharp but broadens by at least 50 nm, and consists of the domains of c-Si and a-Si. We produced a c-a interface in a thinner area of a specimen and observed it by high-resolution TEM (Fig. 3), in the same way as described above. Clearly, an isolated amorphized area is embedded in the damaged c-Si [Fig. 3(c)] and many fragmented c-Si remain in a translational region closer to the amorphized area [Fig. 3(d)]. This indicates that c-Si becomes a-Si heterogeneously under electron irradiation.

After *in situ* annealing of the irradiated specimen of Fig. 2 at 773 ± 25 K in a 200 keV TEM, recrystallization took place at the a-c interface slightly due to solid-phase epitaxial growth [13]. After subsequent annealing at 823 ± 25 K for 2200 s, a-Si returned to c-Si completely. As well as the epitaxial growth, c-Si particles nucleated and grew in the amorphized area, resulting in polycrystalline Si.

The amorphization is summarized in Fig. 4. The dose needed for amorphization, compiled in Fig. 4, means the

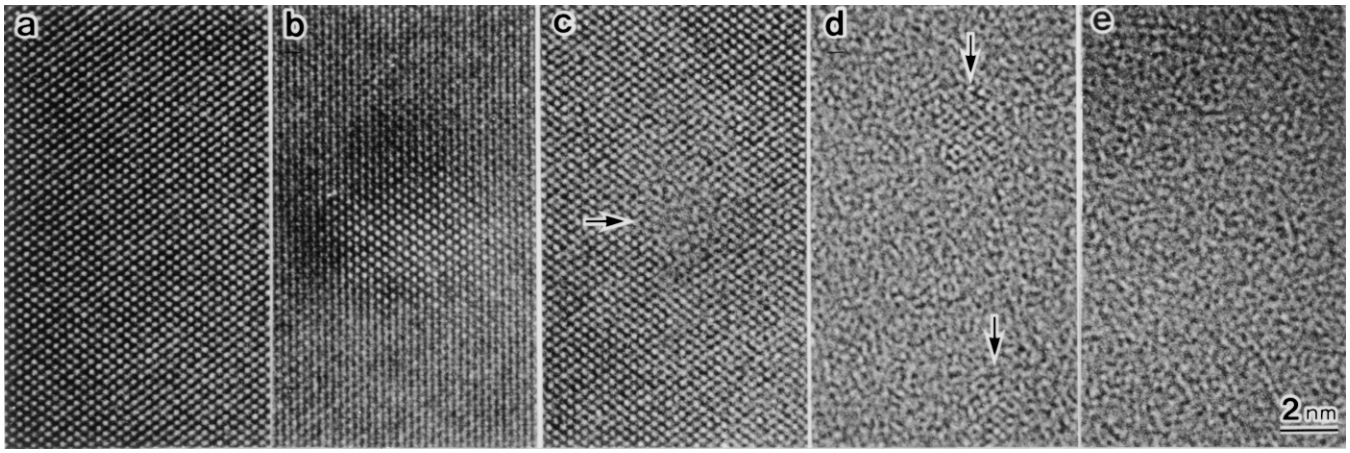

FIG. 3. Structural change with the increase of electron dose from (a) to (e). Postirradiation TEM observation. (a) Damaged c-Si; (b) damaged c-Si with an irradiation-induced defect of about 6 nm in diameter; (c) a localized a-Si (indicated by an arrow); (d) the fragmented c-Si in a-Si (indicated by arrows); and (e) a-Si. ($E = 2$ MeV, $T = 25$ K, $\phi = 1.0 \times 10^{20}$ cm^{-2} s^{-1}, the average dose, $D = 4.8 \times 10^{22}$ cm^{-2}.)

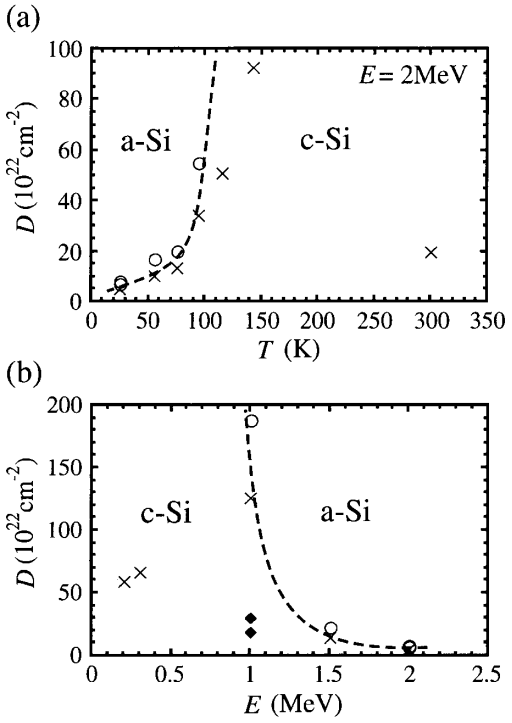

FIG. 4. Silicon structures under electron irradiation as a function of dose D and irradiation temperature T in (a) and that of D and electron energy E in (b). Circles and crosses represent amorphous and damaged crystal, respectively. All the data in (a) were obtained by 2 MeV electron irradiation. Data in (b) were obtained at 25 ± 5 K, except that the data of $E = 0.2$ and 0.3 MeV were taken at about 15 and 4.2 K, respectively, and the data from Ref. [5] (indicated by diamonds) were taken below 10 K.

dose when the central area of approximately 300 nm in diameter turned white in bright-field TEM images without any residual contrast due to fragmented c-Si. The amorphization by electron irradiation is observed in lower temperatures [Fig. 4(a)] than that by ion implantation [14]. It is likely that the athermal migration of point defects [15] is more promoted under electron irradiation than ion implantation, and recovers the crystallinity even at the lower temperatures, thereby lowering the critical temperature of amorphization below that in ion implantation. It is more likely that low-energy recoils at the a-c interface cause crystallization and the process is thermally assisted, as shown by simulation [16] and the experimental work [5]. The dose needed for amorphization increases steeply with the decrease of electron energy [Fig. 4(b)]. The previous experiment [5] which attempted to amorphize c-Si by electron (1 MeV) irradiation, indicated by the diamonds in Fig. 4(b), never contradicts the present data. The amorphization by electron irradiation in Si turns out to need both the low temperatures and the high electron energies.

It is well known that a Frenkel pair, i.e., a pair of a self-interstitial and a vacancy, is introduced by the irradiation of electrons when their energies exceed only about 0.16 MeV and that the clustering of point defects occurs under electron irradiation at low temperatures due to the athermal migration. The accumulation of point defects and their clusters is therefore insufficient to account for the amorphization under electron irradiation, in contrast to the homogeneous amorphization [7] by light-ion implantation. With the increase of electron energy, the production rate of a cluster of point defects via a single collision event increases: In fact, the production rate of divacancies at 1.5 MeV with the $\langle 110 \rangle$ incidence is approximately 3 to 3.5 times larger than that at 1.0 MeV [17]. Comparing the dose needed for amorphization as a function of E [Fig. 4(b)], we suggest that the complex collision events, which create extremely small cascades such as divacancies, are crucially needed for the amorphization. The threshold electron energy for amorphization probably exists slightly below 1 MeV at 25 K, which corresponds to about 150 eV of the maximum energy transfer from an electron to a primary knockon atom. To our knowledge, the corresponding energy in ion implantation has never been determined from experiments. In some accordance with the present data, a classical molecular dynamics study has suggested that heterogeneous amorphization occurs when the recoil energy of a primary knockon atom exceeds the threshold value between 50 and 200 eV at 80 K [18].

It is generally described that transformation from crystal to amorphous takes place whenever the average squared displacement of atoms from their equilibrium positions reaches a critical value [19]. It is also known that electron irradiation renders various compounds into amorphous [20], while it hardly does the elemental materials. These imply that a specific defect configuration exists in Si that possesses a certain lifetime during electron irradiation. Accumulation of these defects increases the *static* average squared displacement monotonously with dose, naturally leading to amorphization. Self-interstitials and their clusters have already been suggested as embryos of a-Si [5,6,20]. In fact, a self-interstitial [21] with the Jackson configuration [22] and a pair of di-interstitials and a divacancy [6] were examined theoretically, since the models include odd-membered atom rings that a-Si probably contains [23]. However, self-interstitials are movable under electron irradiation even at the amorphization temperatures [14], and the pair of a divacancy and a di-interstitial was introduced by a somewhat artificial manner in the simulation [6]. The models are therefore evolved with the recently proposed clusters of four self-interstitials, i.e., I4 [24], which consist of 5-, 6-, and 7-membered rings without any dangling bonds. We suggest that the clusters of four self-interstitials form heterogeneously via the complex collision events and the accumulation of the clusters with dose induces amorphization. The well known clusters of self-interstitials, i.e., the {113} defects also contain odd-membered rings. However, the environment in Si crystal, where the one-dimensionally periodic structure of the {113} defect

[25] can be formed, presumably prevents amorphization [Fig. 1(a)]. It is known that a-Si is produced by indentation [3] or surface scratch [4]. Knowing that self-interstitials are left in c-Si after the unload as described in a theoretical study [26], one may also relate the amorphization under stress to the clustering of self-interstitials. On the other hand, the clusters of vacancies are unlikely to contain odd-membered rings in their structures [27], so they do not seem amorphous embryos.

A number of defects of a few nm in diameter were introduced as seen in Figs. 1(a), 2(b), and 3(b). The similar defects were observed by TEM in c-Si irradiated by low-energy (0.65 MeV) electrons below 35 K [28] and near a c-a interface produced by ion implantation [29]. Similar to the behavior of the defects produced by ion implantation [29], a considerable part of the defects, introduced by 2 MeV electron irradiation at 25 K, remained after annealing at 823 ± 25 K for over 7200 s, while an amorphized region of over 300 nm in diameter returned to c-Si more promptly at the same temperature, as is mentioned above. Large cascades or directly created amorphized areas, which are assumed in heterogeneous amorphization [1] by heavy-ion implantation, are unlikely to appear in electron-irradiated Si. So, the defects, which possibly contain vacancies, do not seem correlated with the amorphization directly.

In conclusion, we have found that a new route exists for amorphization in Si. We have discussed the mechanism of amorphization in Si in the light of our experimental results. Finally, the amorphization under electron irradiation may be useful for fabricating various artificial Si structures for optical and electronic transport applications.

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