IEICE TRANSACTIONS

on Electronics

VOL. E99-C NO. 4
APRIL 2016

A PUBLICATION OF THE ELECTRONICS SOCIETY

The Institute of Electronics, Information and Communication Engineers
Kikai-Shinko-Kaikan Bldg., 5-8, Shibakoen 3chome, Minato-ku, TOKYO, 105-0011 JAPAN

PAPER

Low-Temperature Activation in Boron Ion-Implanted Silicon by Soft X-Ray Irradiation

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SUMMARY A novel activation method for a B dopant implanted in a Si substrate using a soft X-ray undulator was examined. As the photon energy of the irradiated soft X-ray approached the energy of the core level of Si 2p, the activation ratio increased. The effect of soft X-ray irradiation on B activation was remarkable at temperatures lower than 400°C. The activation energy of B activation by soft X-ray irradiation (0.06 eV) was lower than that of B activation by furnace annealing (0.18 eV). The activation of the B dopant by soft X-ray irradiation occurs at low temperature, although the activation ratio shows small values of 6.2×10^{-3} at 110°C. The activation by soft X-ray is caused not only by thermal effects, but also electron excitation and atomic movement.

key words: *boron dopant, low-temperature activation, soft X-ray irradiation, sheet resistance, electron excitation, depth profile*

1. Introduction

To realize the ubiquitous world, large-scale integrated circuits embedded with ultra-fine complementary metal-oxide-semiconductor (CMOS) field effect transistors (FET) are essential devices. According to the international technology roadmap for semiconductors, the physical gate length of CMOS FETs needed to be reduced to 13 nm with a corresponding junction depth of 9 nm by 2013 [1]. To achieve this request, the dopant diffusion length has to be suppressed below 1 nm during the activation process.

When the dopant activation is carried out by rapid thermal annealing, transient diffusion with fast velocity sometimes occurs because of point defects produced by ion implantation, and there is a broadening of the tail by approximately 25 nm for annealing at 1050°C [2]. This phenomenon is known as transient enhanced diffusion (TED) and is a limiting factor for scaling down of semiconductor devices. The TED of B with ultra-low energies of 250 to 1000 eV has been reported [3]–[6].

To date, microwave annealing of B-implanted Si [7], laser spike annealing of B ion-implanted Si [8]–[10], and flash lamp annealing [11] have been reported. The process temperature of these annealing methods is too high to form an optimized shallow junction. Therefore, low-temperature activation is required for ultra-shallow junction formation.

We have developed a crystallization method for amorphous Si, Ge, and $Si_{1-x}Ge_x$ in a low-temperature range using soft X-ray irradiation [12]–[17]. The excitation of core electrons by the soft X-ray irradiation enhances local atom movement and enables the low-temperature crystallization. The threshold temperature for crystallization was decreased by approximately 100°C in comparison with conventional furnace annealing. It is expected that the interactions between the soft X-ray and the electron in core levels will be applied to low-temperature activation for the next generation semiconductor process.

In this paper, we have proposed a novel activation method for B dopants at low temperature using a soft X-ray undulator. The photon-energy dependences of the sheet resistance and the B depth profile were investigated. In addition, the activation mechanism using soft X-ray irradiation is discussed by comparison with a conventional activation method (furnace annealing).

2. Experimental

An n-type Si (100) wafer with 8–12 Ωcm (impurity concentration: 4×10^{14} cm^{-3}) was cleaned using HF solution. B ions were implanted in the Si wafer with an energy of 5 keV, a dose of 2×10^{15} cm^{-2} and an implant angle of 7 degrees off. Under this condition, the implantation depth (defined at a B concentration of 1×10^{17} cm^{-3}) was 150 nm.

The soft X-ray was generated by a synchrotron radiation facility, NewSUBARU, using an undulator with a length of 2.28 m [18]. The storage-ring energy was 1.0 GeV. The size of the Si substrate was 20×20 mm^2. The soft X-ray beam size on the sample surface was 7.5 mmϕ. The conditions for soft X-ray irradiation are summarized in Table 1. The pressure during the soft X-ray irradiation was 6×10^{-5} Pa.

The photon energy was controlled by the undulator gap. The photon energy was determined by considering the core electron energy levels of the Si substrate and B dopant.

Table 1 Soft X-ray irradiation conditions for B activation.

Condition	A	B	C
Photon energy (eV)	50 - 250	90 - 115	115
Storage-ring current (mA)	200	250	50 - 250
Irradiation time (min)	15	12	60 - 12

Condition A: Photon-energy dependence in wide range.
Condition B: Photon-energy dependence around the Si 2p level.
Condition C: Storage-ring current dependence (to achieve low-temperature treatment).

Manuscript received November 14, 2015.
Manuscript revised December 22, 2015.
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DOI: 10.1587/transele.E99.C.474

The photon energies were widely varied from 50 to 250 eV (condition A). It is thought that the B activation ratio is related to the electron excitation from the core electron level. The photon energy was then more finely varied, from 90 to 115 eV around the energy level of Si 2p (99.8 eV) (condition B). The photoionization-cross section of Si 2p is 4.9 Mb at 115 eV, and that of B 1s is 1.3 Mb at 200 eV [19]. The dose was fixed at 50 mA h. The dose was defined by the product of storage-ring current and irradiation time (hour). Under a storage-ring current of 100 mA and irradiation time of 0.5 h, the dose was indicated to be 50 mA h.

A sample holder without a heating or cooling system was used in this experiment. The sample temperature during the soft X-ray irradiation was automatically increased by radiant energy (the product of photon energy, photon-flux density, and area) above 200°C. The soft X-ray was produced by the storage ring, and the photo-flux density is proportional to the storage-ring current. Therefore, to reduce the sample temperature, the storage-ring current was decreased from 250 to 50 mA (condition C). In this case, the irradiated photon flux was linearly decreased from 3.2×10^{14} to 6.4×10^{13} photons/s. The units of photon flux and photon-flux density are photons/s and photons/s/mm^2, respectively.

The surface temperature of the B-implanted Si substrate during the soft X-ray irradiation was measured by a pyrometer via a ZnSe window. The measurement wavelength of the pyrometer was in the range of 7.5 to 13 μm. The temperature measured by the pyrometer is influenced by the emissivity of Si and the measurement angle. To determine the validity of the temperature measured by the pyrometer, the temperature was also measured by a thermocouple. In addition, the validity of this emissivity was confirmed from measurement of the Si substrate on a ceramic heater in the range of 100 to 700°C at the same configuration in air. It was confirmed that the emissivity of Si was similar to the reported value (0.6 [20]), and the angle dependence was negligible. Furthermore, the measured sample temperature was not the temperature of the B implanted region. The actual temperature of the B implanted region is important for the activation mechanism. However, it is difficult to measure only the B implanted region. This is a future issue. From a brief estimation, the difference in temperature between the surface and the reverse side of the Si substrate in the steady state was 0.1°C because the thermal conductivity in the Si substrate was large. During the actual sample temperature measurement, the sample temperature became constant after 1 min. In this study, the soft X-ray irradiation times were from 12 to 60 min. The transitional time was short in comparison with the soft X-ray irradiation time. Therefore, the transitional process at the initial stage of soft X-ray irradiation can be considered negligible.

To compare with the conventional method, furnace annealing in a N_2 atmosphere was carried out in the range of 100 to 1000°C for 10 min. In addition, to clarify the differences in B depth profile between the soft X-ray irradiation and conventional annealing, the furnace annealed samples were prepared under conditions where the temperature corresponded to the soft X-ray irradiation. The samples were annealed in a furnace at 280 or 500°C for 15 min because the sample temperatures were 240 and 460°C at 115 and 250 eV, respectively.

The sheet resistance was measured by a four-point probe method at room temperature in air. The distance between probes was 1 mm. A correction factor for the sample structure (the relationship between the sample size and the probe distance) was set at 4.54 [21]. The activation ratio was given by the Irvin curve [21] and dopant dose quantity. Although the mobility was changed by the impurity concentration and the crystallinity of the B implanted region, the carrier concentration was estimated using the Irvin curve, which includes the influence of change in mobility. If the defects resulting from implantation damage remained, the actual activation ratio would be higher than the activation ratio estimated using the Irvin curve. In this study, the activation energy (E_a) of B activation was estimated from the Arrhenius plot of the activation ratio, although the influence of defects on mobility is not clear.

The B depth profile was evaluated by secondary ion mass spectroscopy (SIMS). The primary ion specie and accelerating voltage were O_2^+ and 3 kV, respectively. The diameter of the analyzed region was 60 μmϕ. The B depth profile was evaluated using SIMS measurements three times. In this case, the variation of the B concentration around the maximum concentration was approximately 2%. In addition, the precision of the absolute concentration was 10%. The signal-noise (S/N) ratio at a B concentration of 3×10^{16}cm^3 was estimated to be ±30% by the intensity of B (counts). Furthermore, the variation in depth was less than 2 nm.

3. Results

Under condition A, the dependence of the activation on the photon energy and the relationship between the energy levels Si 2p, Si 2s, and B 1s and irradiated photon energy were investigated. In addition, under condition B, the relationship between the energy level Si 2p and irradiated photon energy was investigated in detail. The sheet resistance and the temperature of the sample as a function of soft X-ray photon energy at storage-ring currents of 200 and 250 mA are shown in Fig. 1. At the storage-ring current of 200 mA, the temperature at the photon energy of 115 eV, which corresponds to the energy level of Si 2p core-electrons (99.8 eV), showed the highest value, 460°C. The Si 2p core-electrons were excited by the soft X-ray irradiation and then relaxed, resulting in an increase in the Si substrate temperature. For photon energies above 115 eV, the cross section of Si 2p core-electrons decreased [19]. The number of absorbed photons in the B implanted region decreased, resulting in a decrease in temperature. The sheet resistance was decreased from 8 to 2 kΩ/sq by the soft X-ray irradiation. The curve of sheet resistance was related to the sample temperature, except for the sheet resistance at the photon energy of 200 eV. At the storage-ring current of 200 mA, the sheet resistance was the

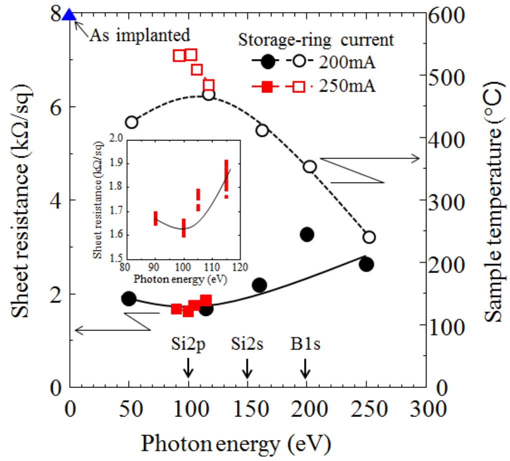

Fig. 1 Sheet resistance (closed symbol) and temperature of Si wafer (open symbol) as a function of photon energy of soft X-ray at storage-ring currents of 200 and 250 mA (conditions A and B). The sheet resistance of as-implanted Si also shows at the photon energy of 0 eV. The sheet resistance of Si wafer irradiated under the condition B for the photon energies from 90 to 115eV is enlarged in insert.

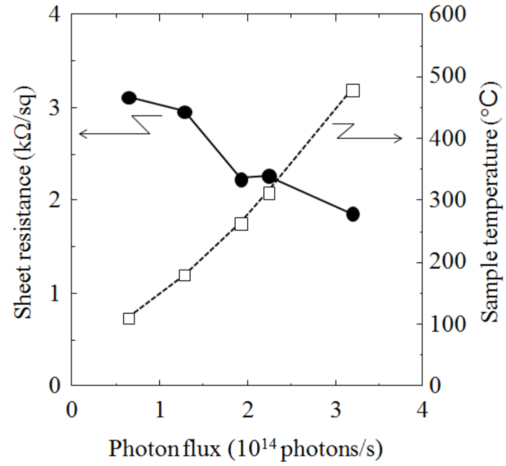

Fig. 2 Sheet resistance and sample temperature as a function of photon flux at a photon energy of 115 eV (condition C).

highest at 200 eV and the lowest at 115 eV. The activation ratios were 1.8×10^{-2} at 115 eV (corresponding to Si 2p) and 5.7×10^{-3} at 200 eV (corresponding to B 1s) for the storage-ring current of 200 mA. When the B atom is substituted for the Si atom in the Si lattice, the B atom forms a hole. Even if the electrons in B 1s were excited by the soft X-ray irradiation, the activation was suppressed because the Si atom did not move and the lattice site of Si was occupied.

Under condition B, to elucidate the dependence of the dopant activation on photon energy because of the electron excitation around the Si 2p energy level, the sheet resistance is shown in Fig. 1. The activation was mostly enhanced at 100 eV. The core level of Si 2p is 99.8 eV. Here, the electron excitation by the soft X-ray irradiation in Si was considered using the following equation. The transition probability (W_{fi}) from an initial state (E_i) to a final state (E_f) is expressed by

$$W_{fi} = \frac{2\pi}{\hbar^2} |H'_{fi}|^2 \delta(E_f - E_i - E_p)$$

where H'_{fi} and E_p indicate the transition moment and the irradiated photon energy. According to this equation including Fermi's golden rule, the electron excitation is enhanced by approaching the energy of the core level ($E_f - E_i$).

The sample temperatures at photon energies of 90, 100, 105, and 115 eV were 526, 528, 504, and 479°C, respectively. The sample temperature dependence of sheet resistance was observed in the range of 479 and 528°C. It is shown that the sheet resistance was related to the sample temperature in the range of 479 and 528°C.

Under condition C, the dopant activation at low temperature was investigated. The sheet resistance and sample temperature as a function of photon flux at a photon energy of 115 eV are shown in Fig. 2. As the storage-ring current was decreased from 250 to 50 mA (the photon flux decreased from 3.2×10^{14} to 6.4×10^{13} photons/s), the sample temperature decreased from 480 to 110°C. The sheet resistance was increased to 3.1 kΩ/sq by decreasing the sample temperature. The sheet resistance of both the as-implanted sample and the annealed sample at 100°C in N_2 atmosphere was 8 kΩ/sq. The activation ratio for the soft X-ray irradiation was estimated to be 6.2×10^{-3} at 110°C. It was confirmed that the dopant activation was achieved by not only thermal effects, but also electron excitation during soft X-ray irradiation.

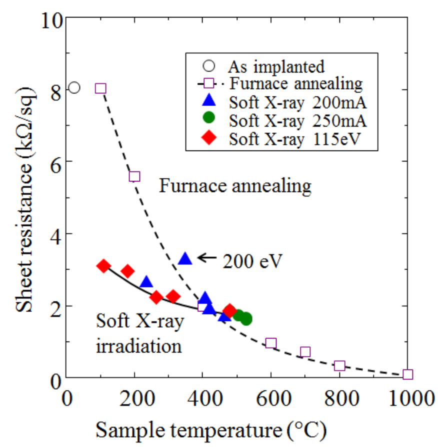

Fig. 3 Sheet resistance as a function of sample temperature. Open symbols show the furnace annealed Si substrate from 100 to 1000°C. Closed triangles, circles, and diamond-shaped symbols show samples treated at conditions A, B, and C in Table 1, respectively. The solid line is used to guide the eye for the sheet resistance of the soft X-ray irradiated samples.

Figures 3 and 4 show the sheet resistance as a function of sample temperature and the relationship between the activation ratio and the reciprocal absolute temperature. A difference between soft X-ray irradiation and furnace annealing was not observed in the range of 400–500°C. However, the sheet resistances of the soft X-ray irradiated samples were lower than that of the furnace annealed samples

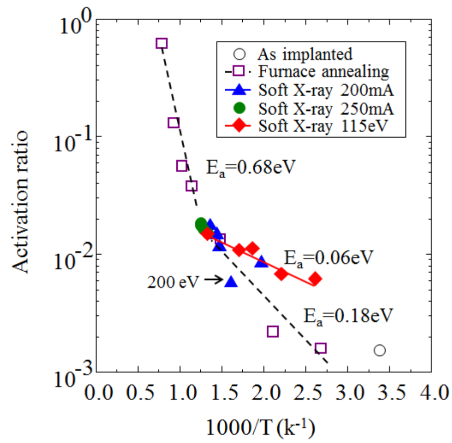

Fig. 4 Relationship between activation ratio and reciprocal absolute temperature. The activation energies of B dopant activation were estimated from these slopes, and the activation energies are summarized in Table 2.

Table 2 Activation energies of B dopant activation with various methods and conditions.

Method	Furnace annealing		Soft X-ray irradiation
Temperature range (°C)	100 – 400	600 – 1000	240 – 460
Photon energy (eV)	–	–	115
Storage-ring current (mA)	–	–	50 – 250*
Activation energy (eV)	0.18	0.68	0.06

*Except the activation ratio at 200eV

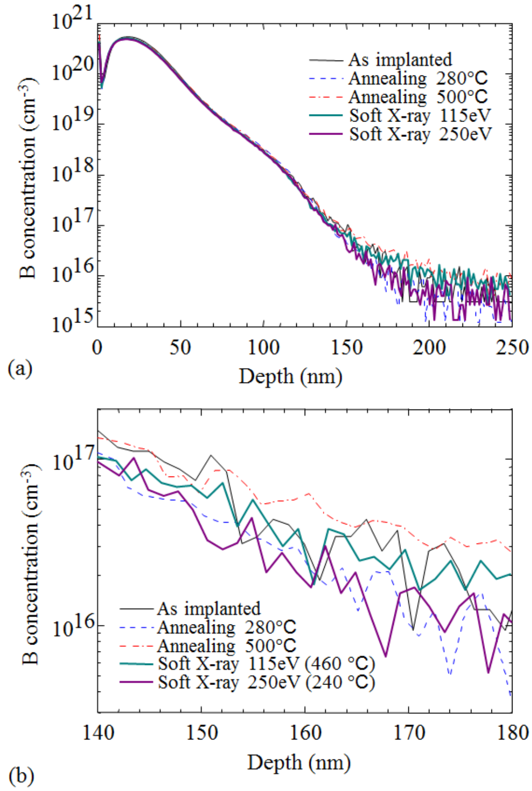

Fig. 5 B depth profile in Si substrate. (a) Soft X-ray irradiated sample at 115 and 250 eV at storage-ring current of 200 mA for 15 min (condition A), and as-implanted and furnace annealed samples at 280 and 500°C for 15 min. (b) Enlarged depth profile in the range of 140 to 180 nm.

below 400°C. Figure 1 suggests that both low sheet resistance and high sample temperature were achieved at the same time. However, the effect of soft X-ray irradiation on the activation was confirmed at low temperature, below 400°C, in Fig. 3. Detailed study of the influence of photon energy on activation ratio without thermal effects is under consideration. The activation energies of the dopant activation estimated from the slope of the Arrhenius plot are summarized in Table 2. For furnace annealing, the degree of the slope changed at 500°C. As mentioned later, this is related to two phenomena (the recovery of crystallinity and B substitution). The activation energies at low- and high-temperature ranges were 0.18 and 0.68 eV, respectively. On the other hand, for soft X-ray irradiation, the activation energy was 0.06 eV, lower than that for furnace annealing. The discrepancy of activation energy between the soft X-ray irradiation and furnace annealing indicates that activation by soft X-ray irradiation is due to not only thermal effects, but also the excitation of the core electrons, followed by local atomic migration.

To estimate the activation energy from the Arrhenius plot of activation ratio, only the sample temperature had to be changed. In this study, the sample temperature was controlled by changing the photon flux. Therefore, the exact activation energy without the influence of different photon fluxes cannot be obtained. Therefore, the exact activation energy and the effect of soft X-ray irradiation on the dopant activation cannot be discussed. Both cooling and heating systems are under construction.

The B depth profiles in the Si substrate irradiated at 115 and 250 eV at the storage-ring current of 200 mA for 15 min are shown in Fig. 5. For reference, the as-implanted and furnace annealed samples at almost same temperature and the same treatment time as the soft X-ray irradiation are also shown in Fig. 5. The dopant diffusion of both samples irradiated with soft X-rays was suppressed compared with the furnace annealed sample in the range of 40 to 130 nm. No significant difference in the diffusion length in all samples was observed in the range of 0 to 130 nm. In the case of annealing at 500°C in N_2 atmosphere, the slight diffusion of B atoms was observed in the range of 140 to 180 nm, as shown in Fig. 5 (b). However, the B depth profiles of other samples were almost the same, and the difference in B concentration was in the range of the S/N ratio (±30%). The X-ray absorption ratios of Si with a thickness of 130 nm at 115 and 250 eV were estimated to be 92% and 75%, respectively [22]. This implies that activation by soft X-ray irradiation was effective in a shallower region than 130 nm because the diffusion length was suppressed below 1 nm.

4. Discussion

Next, we discuss the effect of soft X-rays and the activation mechanism. As the photon energy of soft X-rays approached the energy corresponding to the Si 2p orbital level, the activation was enhanced by the soft X-ray irradiation. The sheet resistance is related to not only the sample temperature, but also photon energy. Therefore, fine tuning of the photon energy is important for effective activation of B dopant in a Si substrate. The sheet resistance after the soft X-ray irradiation strongly depended on the irradiated photon energy. The activation mechanism of B dopant in Si can be explained by the interaction between the soft X-ray and the electrons in the Si 2p level. Therefore, the behavior of Si atoms is important in this activation.

Activation by furnace annealing is caused by the movement of dopant atoms to lattice sites of Si. This process corresponds to the Arrhenius plot for annealing in the high-temperature range, as shown in Fig. 4. For furnace annealing, the substitution of B atoms did not occur at low temperature because Si and B atoms did not have enough energy for atomic migration.

The activation mechanism for soft X-ray irradiation is considered as follows. The behavior of Si and B atoms during the soft X-ray irradiation at low temperature is shown in Fig. 6 (a). In this study, the sample was not carried out

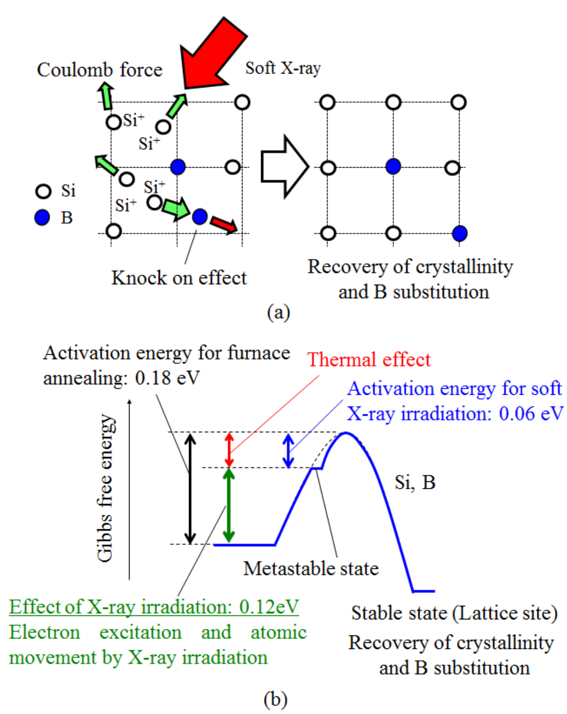

Fig. 6 Effect of soft X-ray irradiation on B activation at low temperature. (a) Schematic diagram of mechanism of low-temperature activation by soft X-ray irradiation. (b) Gibbs free energy and activation energy for furnace annealing and soft X-ray irradiation. Gibbs free energy (G) is expressed as G = H − TS, where H, T, and S are enthalpy, temperature, and entropy, respectively.

preamorphization. However, many interstitials and vacancies were generated near the surface during B implantation. The ionization of Si atoms via excitation of Si 2p core-electrons was generated by the soft X-ray irradiation. In this case, the atomic movement of Si was enhanced by the composited local lattice vibrations. In addition, the ionization produced a Coulomb force between Si atoms. The B atom can shift to the lattice site of Si atom during the recovery of crystallinity in amorphized Si by B ion implantation. The decrease in sheet resistance is due not only to the recovery of crystallinity but also to B substitution (change in B distribution). It is difficult to distinguish the dominant phenomenon from this experiment. This is a subject for future work. The B atoms preferentially were knocked out by the atomic movement of Si because the mass of B atoms is lighter than that of Si atoms and the atomic size of B atoms is smaller than that of Si atoms. Therefore, the B activation may have been caused by the movement of B atoms to the Si lattice site as a result of a knock-on effect. The knock-on effect is one of the candidate mechanisms that explains these experimental results.

Next, the activation was investigated with respect to the activation energy. The Gibbs free energy and the activation energy for furnace annealing and soft X-ray irradiation are shown in Fig. 6 (b). For furnace annealing below 500°C, the sheet resistance was reduced by the recovery of crystallinity [23]. This recovery was caused by thermal energy only. As mentioned above, it is known that the decrease in sheet resistance at high temperature (above 600°C) is produced by B substitution [23]. This phenomenon requires higher thermal energy than the recovery of crystallinity. Here, the activation energy for the soft X-ray irradiation was compared with the activation energy of furnace annealing in the low-temperature region. For furnace annealing, the B activation energy was 0.18 eV in the low-temperature region. In contrast for soft X-ray irradiation, the activation energy was reduced to 0.06 eV. The difference in the activation energy between the furnace annealing and the soft X-ray irradiation, namely, 0.12 eV, may be related to the effect of soft X-ray irradiation. We have reported that a crystal-like region, called the quasi-nucleus, is formed by electron excitation and atomic movement with soft X-ray irradiation of amorphous Si [13]–[16]. It seems that the metastable state (crystal-like region) in the damage region introduced by B ion implantation was achieved by soft X-ray irradiation. The activation energy of 0.06 eV may be related to the thermal energy of the transition process from the metastable state to the stable state (lattice site). The amorphized layer was recovered by soft X-ray irradiation in spite of the low-temperature treatment. Therefore, the activation energy was small in comparison with conventional furnace annealing. We speculate that the metastable state can be realized through soft X-ray irradiation techniques, as shown in Fig. 6 (b). Although there is no evidence for the metastable state, this concept is one of the candidate mechanisms that explains these experimental results.

5. Conclusions

The photon-energy dependence of sheet resistance and the activation mechanism for soft X-ray irradiation were investigated. The activation ratio was increased by approaching the core level of Si 2p. In contrast, the activation was not enhanced by soft X-ray irradiation at a photon energy corresponding to B 1s. The effect of soft X-ray irradiation on the sheet resistance was remarkable below 400°C. Activation of the B dopant occurred at 110°C, although the activation ratio showed a small value of 6.2×10^{-3}. The B activation energy with soft X-ray irradiation was lower than that with furnace annealing. The soft X-ray activation was caused not only by thermal effects, but also by electron excitation and atomic movement.

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