

**ULTRAVIOLET RAMAN SPECTROSCOPIC STUDY ON
FLASH-ANNEAL RECRYSTALLIZATION OF ULTRA-SHALLOW
BORON-IMPLANTED LAYER ON SILICON**

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Non-destructive characterization of the recrystallization process in ultra-shallow B- or BF₂-implanted layers with pre-amorphization implantation of Ge on silicon was performed by Raman scattering spectroscopy utilizing multiwavelength ultraviolet (UV) excitation. To recrystallize damaged layers, a short-time annealing was carried out in a novel millisecond flash anneal system. By making use of the shallow penetration depth of UV light in silicon, we can distinguish Raman signals of single- and poly-crystalline, and amorphous silicon from the ultra-shallow region at depths of several nanometers from the surface. Depth profiles of B, F and Ge atoms were measured using secondary ion mass spectroscopy (SIMS) before and after annealing. The Raman observations are correlated with the diffusion characteristics measured by SIMS and sheet resistance. The ultraviolet Raman spectroscopy is found to be a very powerful tool to characterize the formation of ultra-shallow junction.

INTRODUCTION

Ultra-shallow junction formation is a key issue with the shrinkage in the device dimensions beyond the 90 nm node. Effective electrical activation of a dopant without significant diffusion is definitely required for the very thin ion-implanted layer. Rapid thermal annealing (RTA) using tungsten halogen lamps is a very popular approach for a short time annealing [1, 2]. To improve current technology combining ion implantation and anneal, a very rapid anneal (<10 ms) at a very high temperature (>1100°C) is considered to be promising for ultra-shallow junction formation. For this purpose, instantaneous photon irradiation using an excimer-laser or non-filament based arc lamp has been intensively studied for the short time annealing [3-7]. In our group, a novel millisecond flash anneal system using multiple Xe arc-flash lamps has been developed to achieve the very short-time surface heating [8].

The effects of annealing are usually examined in terms of sheet resistances measured by a four-point probe and depth profiles of dopants. Understanding the material properties for an ultra-thin layer with a thickness less than a few tens of nanometers is

essential to engineering development of the ultra-shallow junction. Although recrystallization of the implanted layer is a key issue, there has been no clear observation of the recrystallization process for ultra-shallow junction formation.

In this paper, the recrystallization process in a low-energy boron-implanted layer by annealing was non-destructively characterized by means of Raman scattering spectroscopy with ultraviolet (UV) excitation. For recrystallization annealing was carried out in the novel millisecond flash anneal system. The Raman signal related to recrystallization of the shallow region is acquired within several nanometers from the surface by making use of the shallow penetration depth of the UV light for Si. The results are compared with diffusion characteristics measured by secondary ion mass spectroscopy (SIMS) and sheet resistance.

EXPERIMENT

$^{11}\text{B}^+$ or $^{49}\text{BF}_2^+$ ions were implanted into 300-mm-diameter p-type Si(100) wafers with a resistivity of $\sim 10 \Omega\cdot\text{cm}$ with dose levels of 1×10^{15} or $1.5 \times 10^{15} \text{ cm}^{-2}$. The only difference that was observed between samples with different dose levels was the B concentration that changed in accordance with the dose level. Thus, only the results regarding samples with the dose level of $1 \times 10^{15} \text{ cm}^{-2}$ are described in this report. The implantation energy were adjusted at 1 and 3 keV for B^+ and BF_2^+ ion implantations, respectively. Prior to B^+ or BF_2^+ ion implantation, germanium ions were implanted for pre-amorphization with an implantation energy of 5 keV and a dose level of $1 \times 10^{15} \text{ cm}^{-2}$.

Implanted wafers were annealed in the novel millisecond flash annealing system [8] under one atmospheric pressure air. The flash annealing system consists of arrays of Xe arc flash lamps and a hot plate for pre-heating and the duration of the flash was controlled around 1 ms. The pre-heating temperature was kept at 465°C . The spectrum of the light emitted from the flash lamp shows a maximum intensity at a wavelength between 0.3 and 0.4 μm that is much shorter than the absorption edge of Si. Light absorption in a shallow region with a millisecond-scale flash duration makes selective surface heating possible without critically heating the bulk Si. Since it is very difficult to measure the wafer transient surface temperature, the input power to the system, denoted by 'flash power', was used as a process parameter measurement in this work. The depth profiles of B, F and Ge atoms were measured by SIMS.

Raman spectra of the implanted sample's surface before and after flash anneal were measured at room temperature using a Raman microscope in the backscattering geometry mode. A 514.5-nm Ar^+ laser, a 363.8-nm Ar^+ laser and the fourth harmonic (266.0 nm) of a Nd:YAG laser were used as excitation light sources. Since both the incident light and Raman signal are attenuated in a sample, half the value of inverse of absorption coefficient is often considered to be the penetration depth in Raman spectroscopy. Based on absorption coefficients of 2.03×10^6 , 9.95×10^5 and $1.47 \times 10^4 \text{ cm}^{-1}$ for Si at the wavelengths of 266.0, 363.8 and 514.5 nm, respectively, the penetration depth under excitation at wavelength of 266.0, 363.8 and 514.5 nm are estimated to be

~2.5, ~5 and ~300 nm, respectively. While the optical absorption coefficient of single-crystalline Si is well-established, deterioration of crystallinity with poly-crystallization and amorphization sometime causes widening of its bandgap. Hence, ultra-shallow regions within 2.5~5 and 5~10 nm from the surface is considered to be probed by Raman spectroscopy with excitation by ultraviolet light with wavelengths of 266.0 and 363.8 nm, respectively.

RESULTS AND DISCUSSION

Recrystallization of B⁺-implanted layer

Figure 1 shows SIMS depth profiles of B⁺-implanted wafers annealed by the novel millisecond flash annealing system together with the profile of the as-implanted sample. The input power to the flash power was adjusted at 80% or 100%. As noted in Fig. 1 (a), a slight diffusion of B atoms into the bulk region is observed as the flash power

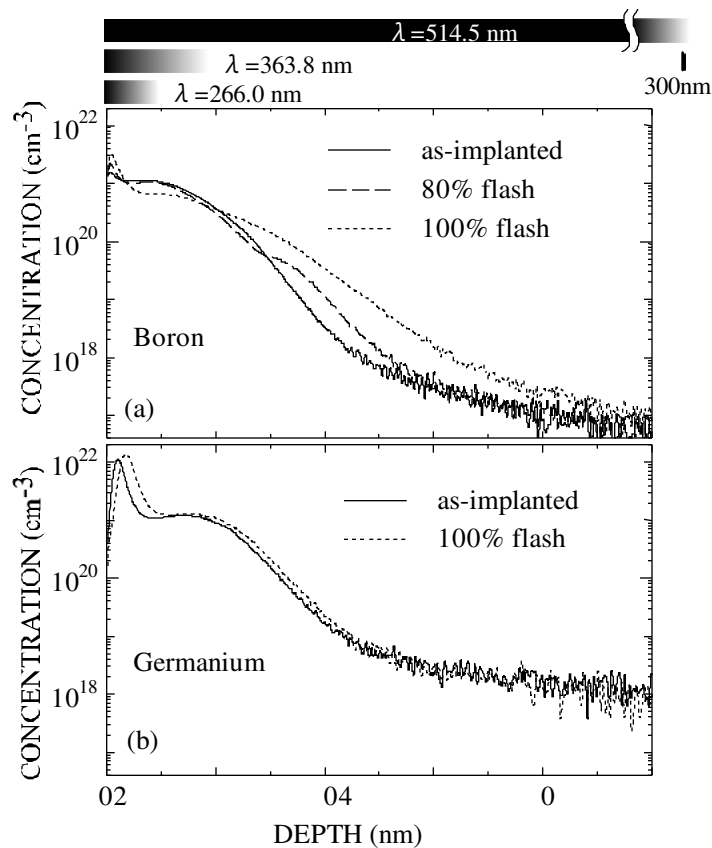


Figure 1. (a) B and (b) Ge depth profiles in B⁺-implanted sample before and after flash anneal measured by SIMS. Crossbars above the figures indicate the region depth observed by Raman scattering spectroscopy under excitation at various wavelengths.

increases. The reference B depth is defined as the depth at which the B concentration is $1 \times 10^{18} \text{ cm}^{-3}$ and is noted to increase from 24 to 32 nm. While no significant Ge movement is observed for Ge atoms located deeper than 7 nm from the surface, Ge atoms accumulated 1 nm deeper after the flash anneal (Fig. 1(b)). Concurrently, the maximum Ge concentration slightly increases after flash anneal, indicating Ge segregation.

Since B atoms are implanted into p-type Si wafers, the implanted layer is not electrically isolated from the bulk region. However, the sheet resistance is considered to be a measure of boron activation due to the large difference in B concentration between the implanted layer and the bulk Si. Here, the background carrier concentration in the bulk Si is estimated to be $\sim 1.0 \times 10^{15} \text{ cm}^{-3}$ based on the bulk resistivity of $\sim 10 \text{ } \Omega \cdot \text{cm}$. Furthermore, in an ultra-shallow p⁺/n structure, poor electrical isolation due to junction leakage and/or punch-through of probes into the n-type substrate often make it difficult to correctly evaluate the sheet resistance. Sheet-resistance measurement of p⁺-layer on p-type Si can avoid the uncertainty observed in measuring an ultra-shallow p⁺/n structure. The sheet resistance measured using a four point probe was evaluated to be 112 ohm/sq. after 80% flash anneal. The sheet resistance decreased to 103 ohm/sq. by increasing flash power to 100%, indicating improvement in dopant activation without significant dopant diffusion.

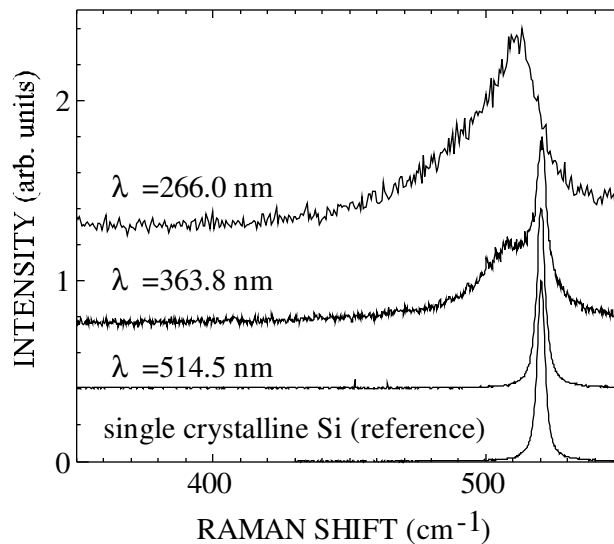


Figure 2. Raman spectra of a B⁺-implanted sample flash-annealed at 100% power with excitation at wavelengths of 266.0, 363.8 and 514.5 nm. Raman spectrum of Si wafer without ion-implantation is shown as a reference.

Figure 2 shows Raman spectra of B⁺-implanted sample annealed with 100% flash power. Under the excitation at a wavelength of 514.5 nm, no difference is observed for the principal Raman peak at 520 cm^{-1} between the implanted sample and bulk Si. The Raman signal from the single-crystalline region beneath the implanted layer obscures the signal from the implanted layer due to the deep penetration depth of the light at wavelengths of 514.5 nm. With the excitation at a wavelength of 363.8 nm, the detection

region is within 5~10 nm from the surface, and the Raman spectrum becomes a mixture of signals due to poly-crystalline with a signal at 510 cm^{-1} , and single crystalline Si. While the Raman spectroscopy under the 514.5 nm excitation probes a very large region compared to the implanted layer, the regions in which the B concentration was on the order of 10^{20} cm^{-3} can be characterized with the 363.8-nm excitation as noted by the crossbars of Fig.1. The poly-crystalline phase dominates under the 266.0 nm excitation allowing detection of a region within 2.5~5 nm from the surface. The spectroscopy under the 266.0-nm excitations probes the region in which the Ge atoms tend to pile up.

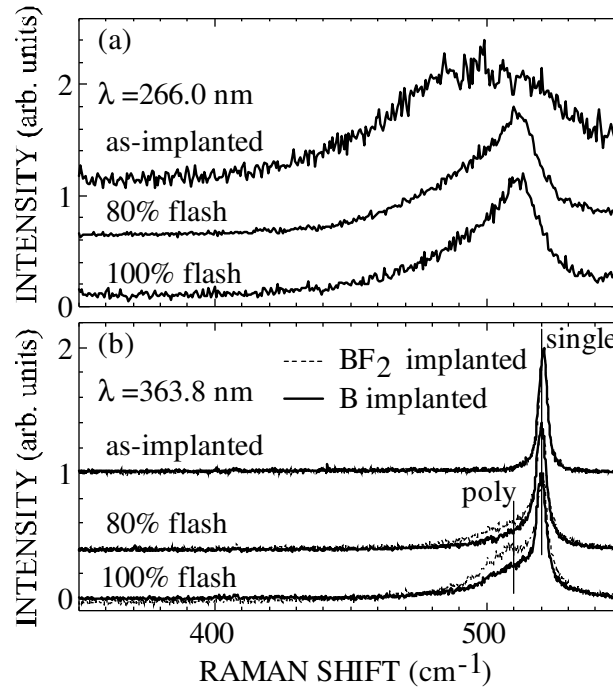


Figure 3. Comparison Raman spectra of B⁺-implanted sample before and after flash anneal measured at excitation wavelengths: (a) 266.0 nm, (b) 363.8 nm. Raman spectra of BF₂⁺-implanted sample are also shown in (b).

Figure 3 shows Raman spectra of B⁺-implanted sample before and after flash anneal. Raman spectra under 266.0-nm excitation indicated that the amorphous phase dominates in a very shallow region within 2.5~5 nm from the surface for the as-implanted sample (Fig. 2(a)). In the amorphous phase, long-distance order longer than 1 nm is destroyed. This results in a broad spectrum caused due to a lack of coherent phonon propagation. After flash anneal, the poly-crystalline phase was detected at a wavenumber of 510 cm^{-1} but the single-crystalline phase was not observed at a wavenumber of 520 cm^{-1} . By taking into account the peak position (510 cm^{-1}) and full-width-of-half-maximum (30 cm^{-1}) [9], the grain size of poly-Si is estimated to be several nm to 10 nm. No difference is observed for the poly-Si Raman peak regardless of flash power, indicating that the recrystallization process from amorphous to poly-crystalline is saturated in the region within a distance of 2.5~5 nm from the surface.

For Raman spectroscopy with 363.8-nm excitation, the observed region is within 5~10 nm from the surface (Fig.3 (b)), and only the Raman peak due to single crystalline Si is observed at 520 cm^{-1} . By carefully examining the spectrum between 420 and 520 cm^{-1} (not shown here), a weak broad signal due to an amorphous phase was observed. For the annealed sample, the Raman signal of poly-crystalline phase was detected together with the signal of single-crystalline phase. The intensity of poly-crystalline signal increased with an increase in the flash power, indicating an increase in the volume of poly-crystalline phase in the region within 5~10 nm from the surface. Presumably, poly/single interface moves deeper with an increase in flash power as shown in Fig. 4. The authors believe that the shift of the poly/single interface to the Si bulk causes the shift of the Ge accumulation toward the bulk Si as shown in Fig. 1(b).

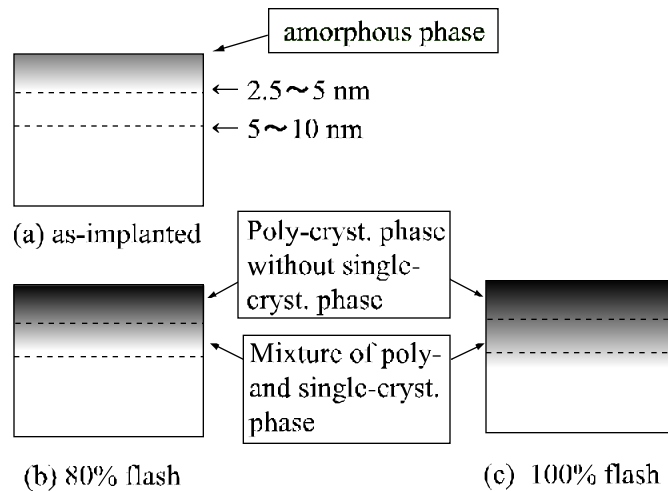


Figure 4. Schematic diagram of recrystallization of boron-implanted layer by flash anneal.

While the maximum Ge concentration exceeds $1 \times 10^{22}\text{ cm}^{-3}$, no Raman signal related to Ge atoms was detected in the Raman observation under excitation at a wavelength of 266.0 nm including probing the region in which Ge atoms pile up. The Raman signal ascribed to Ge-Ge and Ge-Si bonds are expected to be located at wavenumbers between 300 and 400 cm^{-1} . Because the Raman system using 266-nm excitation does not cover the wavenumbers less than 350 cm^{-1} , we cannot judge existence or absence of Ge-related Raman peaks.

Recrystallization of BF_2^+ -implanted layer

The Raman spectroscopy evaluation was carried out for the BF_2^+ -implanted sample. Figure 5 shows the SIMS depth profiles of BF_2^+ -implanted flash-annealed wafers together with the profile of the as-implanted sample. Boron atoms diffused slightly into the bulk silicon from a depth of 17 to 28 nm as shown in Fig. 5(a). The sheet resistance was measured to be 121 ohm/sq. for the sample annealed by 80% flash power. The sheet resistance decreased to 106 ohm/sq. for the sample annealed by 100% flash power, indicating improvement in dopant activation without significant dopant diffusion.

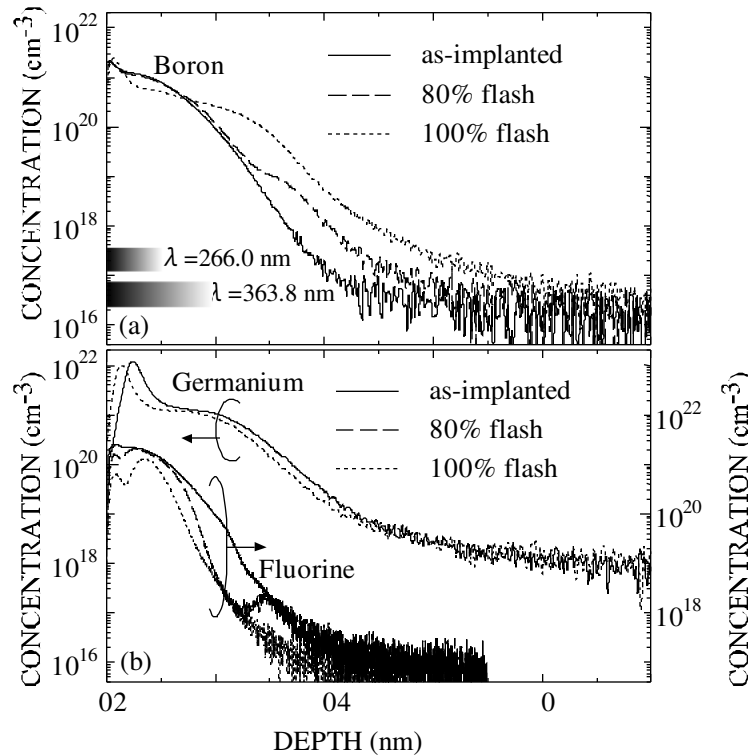


Figure 5. (a) B, (b) Ge and F depth profiles in BF_2^+ -implanted sample before and after flash anneal measured by SIMS. Both horizontal scales of (b) are differentiated for discrimination between F and Ge profiles.

The accumulated Ge atoms at depth of 3 nm from the surface for the as-implanted sample move to the surface after flash anneal as shown in Fig. 5(b). It is noted that the shift is opposite in direction compared to the accumulated Ge for the B^+ -implanted sample after flash anneal as shown in Fig. 1(b). Depth profiles of fluorine after the flash anneal were separated into two peaks at depths of 1 and 3.5 nm from the surface. The separation of F profiles is reported for the flash annealed sample [10]. While the F concentration segregated to a depth of 3.5 nm is kept constant or slightly decreases, the F concentration segregated to a depth of 1 nm distinctly decreases as flash power increases from 80% to 100%. This implies that the segregated F at the depth of 1 nm diffuses to the surface during flash anneal, followed by desorption from the surface. The shift toward the surface of the accumulated Ge is believed to be strongly correlated to the diffusion of F to the surface.

In Raman spectroscopy with 266.0-nm excitation allowing observation of the region within 2.5~5 nm from the surface, the observed spectra (not shown here) was very similar to the spectra shown in Fig. 3(a). In addition to the existence of the large amount of F, on the order of 10^{22}cm^{-3} , the diffusion behavior of Ge atoms in the BF_2^+ -implanted sample is different from the behavior in the B^+ -implanted sample. In comparing the Raman spectra (Fig. 3 (b)) from the two implanted samples, the recrystallization process in the Ge-accumulated region appears to be very similar.

In the Raman spectra under 363.8-nm excitation (Fig. 3(b)), the poly-crystalline phase is observed in the BF_2^+ -implanted sample after flash anneal as in the B^+ -implanted sample. The intensity of polycrystalline phase for BF_2^+ -implanted sample is larger than that of B^+ -implanted sample. By taking into account that the B profile for BF_2 -implanted sample (Fig. 5(a)) is shallower than that of B^+ -implanted sample (Fig. 1(a)), the intense peak of poly-crystalline phase suggests enhancement of polycrystalline formation for BF_2 -implanted sample.

SUMMARY

The recrystallization process for ultra-shallow B- or BF_2 -implanted layers on silicon was characterized by Raman scattering spectroscopy under UV excitation. Ultra-shallow regions of 2.5~5 and 5~10 nm from the surface can be probed under UV excitation at wavelengths of 266.0 and 363.8 nm, respectively. Implanted wafers were annealed in the novel millisecond flash annealing system consisting of an array of Xe arc flash lamps with a hot plate for pre-heating. The near-ultraviolet light absorption within a shallow region with millisecond-scale flash anneal makes selective surface heating possible without critically heating the bulk Si. For both B- or BF_2 -implanted layers, the process from amorphous to poly-crystalline was saturated in the region within a distance of 2.5~5 nm from the surface regardless of flash power. The poly/single interface in the implanted layer moves deeper with an increase in flash power. The intense peak of poly-crystalline in the BF_2 samples to that of the B-implanted sample suggests enhancement of poly-crystallization for the BF_2 -implanted sample. The UV Raman spectroscopy is a powerful tool to understand the recrystallization process for an ultra-thin layer with a thicknesses of less than a few tens of nanometers, and to engineer the development of ultra-shallow junction.

REFERENCES

1. D. C. Jennings, G. de Cock and M. A. Foad, Proc. 6th Int. Conf. on Advanced Thermal Processing of Semiconductors – RTP'98, (1998) 187
2. A. Jain, Electrochemical Soc. Proc. **PV 2000-9**, (2000) 33.
3. S. Talwar, Y. Wang, C. Gelatos, Electrochemical Soc. Proc. **PV 2000-9**, (2000) 95.
4. R.S. Tichy, K. Elliott, S. McCoy and D. Sing, Proc. 9th Int. Conf. on Advanced Thermal Processing of Semiconductors – RTP 2001, (2001) 87.
5. T. Ito, T. Inuma, A. Murakoshi, H. Akutsu, K. Suguro, T. Arikado, K. Okumura, M. Yoshioka, T. Owada, Y. Imaoka, H. Murayama and T. Kusuda, *Jpn. J. Appl. Phys.*, **41** (2002) 2394.
6. W.S. Yoo and K. Kang, Electrochem. Soc. Proc., **PV 2003-14** (2003) 111.
7. S. Talwar, D. Markle and M. Thompson, *Solid State Technology*, **46** (2003) 83.
8. W.S. Yoo and K. Kang, Electrochem. Soc. Proc., **PV 2004-01** (2004) 3.
9. I.H. Campbell and P. M. Fauchet, *Solid State Commun.*, 58 (1986) 739.
10. W.S. Yoo, T. Fukada, T. Setokubo, K. Aizawa and T. Ohsawa, *Jpn. J. Appl. Phys.*, **42** (2003) 1123.

KEY WORDS

1. ultra-shallow implantation
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4. recrystallization
6. dopant diffusion

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