

## Detection of oxidation-induced compressive stress in Si(100) substrate near the SiO<sub>2</sub>/Si interface with atomic-scale resolution

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### Abstract

The angle-resolved Si 2*p* photoelectron spectra arising from transition layer formed between bulk SiO<sub>2</sub> and bulk Si(100)-substrate were measured with probing depth of nearly 2 nm. It was found that the oxidation-induced chemical structures are formed on the Si substrate side of the interface. Furthermore, a part of the oxidation-induced chemical structures in the Si substrate near the interface was found to be closely correlated with the oxidation-induced compressive stress near the interface detected by UV Raman spectroscopy.

### Introduction

The chemical structure of a compositional transition layer (hereafter referred to as CTL) formed on a Si(100) surface significantly affects the performance of Si-based devices [1] and has been studied in detail by angle-resolved photoelectron spectroscopy (ARPES) [2]. It was also found from ARPES study that the oxidation-induced chemical structures appear in the Si substrate near the CTL/Si interface (hereafter referred to as interface) [2]. The stress in the Si substrate has been studied extensively because of its significant effect on the stability of the interface structure [3]. Recently, the stress in the Si substrate near the interface was successfully detected with a probing depth of 5 nm by ultraviolet (UV) excited Raman spectroscopy to reveal the difference between the stress in the Si substrate near the interface and that in the bulk Si [4]. However, the stress distribution in the Si substrate near the interface was not clarified yet with an atomic-scale depth resolution. In this paper, it will be shown that one of the oxidation-induced chemical structures in the Si substrate near the interface detected by ARPES can be correlated with the oxidation-induced compressive stress (hereafter referred to as stress) in the Si substrate near the interface detected by UV Raman spectroscopy and the stress distribution in the Si substrate can be studied by high-resolution Rutherford backscattering (HRBS) [5].

### Experimental Details

The following four types of device-grade oxide film were prepared on the cleaned Si(100) substrates with surface microroughness (*R<sub>a</sub>*) of less than 0.08 nm: 1) The oxide films with *t* = 2.14, 1.41, and 1.67 monolayer (ml), in which the CTLs are stabilized by more than 1 ml of SiO<sub>2</sub>,

were formed by oxidation in a dry O<sub>2</sub> at 900, 1000, and 1050 °C, respectively. Here, *t* denotes the thickness of the SiO<sub>2</sub> layer formed on the CTL. 2) An oxide film with *t* = 2.27 ml was formed by the oxidation in dry O<sub>2</sub> at 900 °C followed by annealing in H<sub>2</sub> (10%)/N<sub>2</sub> (90%) mixture ambient at 400 °C for 20 min (hereafter referred to as FGA). Si 2*p*<sub>3/2</sub> spectra were measured using a high photon flux with the photon energy of 1050 eV available at SPring-8. Other analytical details were described elsewhere [2].

### Experimental Results and Discussion

Figure 1(a) shows the 1050-eV-photon excited Si 2*p*<sub>3/2</sub> spectra measured at photoelectron take-off angles (TOAs) at vacuum/oxide interface of 15° and 85° arising from the oxide film (*t* = 0.91 ml) formed in dry O<sub>2</sub> at 900°C [2]. Figure 1(b), in which the spectra arising from Si-O<sub>4</sub> (Si<sup>4+</sup>), Si-Si-O<sub>3</sub> (Si<sup>3+</sup>), Si<sup>v+</sup>, Si<sub>2</sub>-Si-O<sub>2</sub> (Si<sup>2+</sup>), Si<sup>ii+</sup>, Si<sub>3</sub>-Si-O (Si<sup>1+</sup>), Si substrate (Si<sup>0</sup>), α-Si, β-Si, and γ-Si are resolved, is obtained by taking difference between two spectra in Fig. 1(a), to eliminate the spectrum arising from Si<sup>0</sup> after multiplying the spectrum measured at a TOA of 85° by an appropriate factor [2]. Here, the binding energy of Si<sup>0</sup> is equal to that of bulk Si and α-Si, β-Si, and γ-Si were found to originate from the Si substrate [2]. By self-consistently analyzing the dependence of ten kinds of Si 2*p*<sub>3/2</sub> spectra shown in Figs.

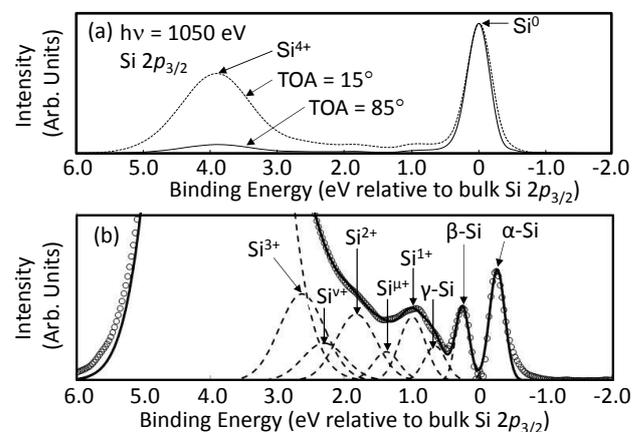


FIG. 1. (a) Si 2*p*<sub>3/2</sub> spectra arising from interface formed in dry O<sub>2</sub> at 900 °C measured at photon energy of 1050 eV and photoelectron take-off angles (TOAs) of 15° and 85°, (b) spectrum obtained by taking difference between two spectra in (a) to eliminate spectrum arising from Si<sup>0</sup>.

1(a) and 1(b) on TOA, the following results are obtained for four types of oxide film [2]. 1) the interface structures are almost the same. 2)  $\gamma$ -Si is localized in the 2nd Si layer from the interface.  $\alpha$ -Si is localized in the 1st Si layer from the interface formed in dry O<sub>2</sub> at 900 °C with and without FGA, while  $\alpha$ -Si is localized in the 2nd Si layer from the interface formed in dry O<sub>2</sub> at 1000 and 1050 °C. In the following it is assumed that  $\beta$ -Si is localized not only in the 3rd Si layer from the interface but also in the 4th Si layer from the interface.

Figure 2 shows the influence of oxidation-temperature on the UV excited Raman peak shifts and the amounts of  $\alpha$ -Si,  $\beta$ -Si, and  $\gamma$ -Si. Here, for the UV Raman spectroscopy the 7-nm-thick oxide films were formed on atomically flat Si(100) surfaces [5] and the Raman peak shifts measured with a probing depth of 5 nm were found to be caused by the compressive stress in the Si substrate [4]. According to this figure, there is a close correlation between UV Raman peak shifts and the amounts of  $\beta$ -Si in the 3rd Si layer from the interface and a weak correlation between UV Raman peak shifts and the amounts of  $\beta$ -Si in the 4th Si layer from the interface, while there is no correlation between UV Raman peak shifts and the amounts of  $\alpha$ -Si and  $\gamma$ -Si.

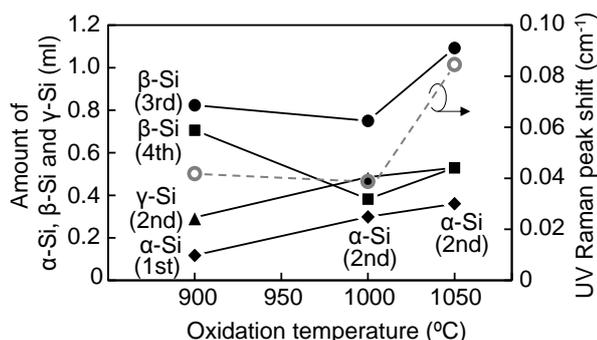


FIG. 2. Dependence of Raman peak shift, amount of  $\alpha$ -Si,  $\beta$ -Si, and  $\gamma$ -Si on oxidation temperature.

Figure 3 shows the influence of FGA on the amounts of  $\alpha$ -Si,  $\beta$ -Si, and  $\gamma$ -Si in the Si substrate formed in dry O<sub>2</sub> at 900 °C. According to this figure, the amounts of  $\alpha$ -Si and  $\gamma$ -Si are slightly influenced by FGA, while the amounts of  $\beta$ -Si in the 3rd and 4th Si layers from the interface are strongly influenced by FGA, in other words, by FGA the amount of  $\beta$ -Si in the 3rd Si layer from the interface decreases extremely and the amount of  $\beta$ -Si in the 4th Si layer from the interface increases extremely.

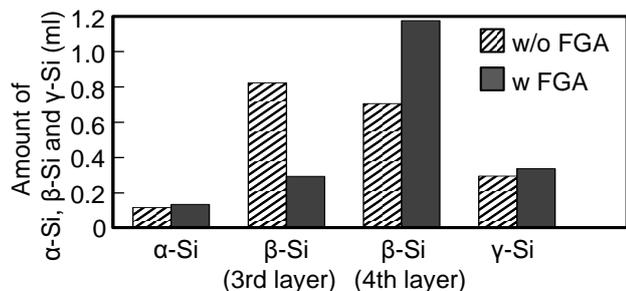


FIG. 3. Influence of FGA on amount of  $\alpha$ -Si,  $\beta$ -Si, and  $\gamma$ -Si in Si substrate covered with the oxide film formed in dry O<sub>2</sub> at 900 °C.

Figure 4 shows a close correlation between the amounts of  $\beta$ -Si in the 3rd Si layer from the interface and UV Raman peak shifts up to nearly 0.04 cm<sup>-1</sup> for three types of oxide film and does not show correlation between the amounts of  $\beta$ -Si in the 4th Si layer from the interface and UV Raman peak shifts. Therefore, the amounts of  $\beta$ -Si in the 3rd Si layer from the interface are closely correlated with the UV Raman peak shifts caused by the compressive stress in the Si substrate [4]. The determination of  $\beta$ -Si distribution in the Si substrate by applying maximum entropy concept [6] to the analyses of 1487-eV-photon excited angle-resolved Si 2p<sub>3/2</sub> spectra is now in progress and will be compared with the stress distribution determined by HRBS. The stress in the 1st and 2nd Si layers from the interface is absent possibly because of the disordered structures of the 1st and 2nd Si layers from the interface, in which Si displacements are larger than 0.009 nm [8].

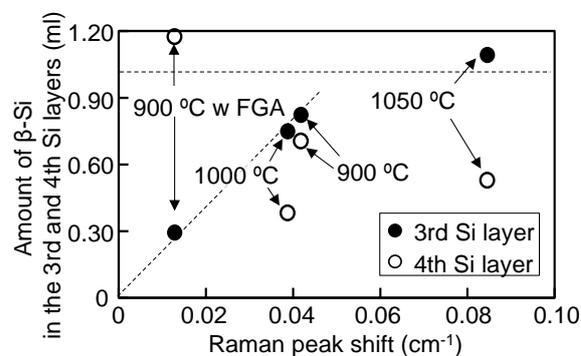


FIG. 4. Correlation between amount of  $\beta$ -Si in the 3rd and 4th Si layers from the interface and UV excited Raman peak shift for four types of oxide film.

### Summary

The amounts of  $\beta$ -Si in the 3rd Si layer from the interface covered with three types of oxide film are closely correlated with the UV Raman peak shifts caused by the oxidation-induced compressive stress near the interface. Therefore, the effect of the dry oxidation step is to induce compressive stress in the 3rd Si layer from the interface in the Si substrate. The stress is subsequently relaxed by FGA.

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### References

- [1] M. L. Green et al., J. Appl. Phys. **90** (2001) 2057.
- [2] T. Suwa et al., Jpn. J. Appl. Phys. **52** (2013) 031302.
- [3] E. Kobera et al., J. Vac. Sci. Technol. B **4** (1986) 720.
- [4] M. Hattori et al., ECS Trans. **19** (2009) 55.
- [5] R. Kuroda et al., IEEE Trans. Electron Devices **56** (2009) 291.
- [6] T. Hattori et al., Microelectron. Reliab. **47** (2007) 20.
- [7] K. Nakajima et al., Jpn. J. Appl. Phys. **45** (2006) 2467.
- [8] A. Bongiorno et al., Phys. Rev. Lett. **90** (2003) 186101.