

## Work-function changes in high-dose B-implanted Si with keV Cs<sup>+</sup> bombardment

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The depth dependence of the relative work-function change ( $\Delta\phi$ ) of 35 keV,  $5 \times 10^{16} \text{ cm}^{-2}$  B<sup>+</sup>-implanted silicon wafers was investigated by considering shifts in the onset of secondary-ion energy distribution under dynamic mode, 14.5 keV Cs<sup>+</sup> bombardment. At the stationary region of Cs surface concentration on the subsurface, the relative  $\Delta\phi$  was found to be 2.6 eV. At the peak region of boron concentration, a further reduction of  $\phi$  by  $\Delta\phi=0.4$  eV was observed, resulting in an enhancement of Si<sup>-</sup> secondary-ion yield. An interface was observed between a complete amorphous layer and defects in this region. It was found that the amount of adsorbed Cs increases up to the interface, and then decreases, eventually reaching a steady-state value. The variation of Cs coverage leads to the work-function change. [S0163-1829(99)02119-0]

### I. INTRODUCTION

There has been enormous interest in the modification of the electronic structure of solids induced by the atoms and molecules adsorbed on surfaces.<sup>1,2</sup> In particular, the fact that the adsorption of alkali metal reduces the work function (WF) of metal and semiconductor surfaces<sup>1-3</sup> has been of practical interest for scientific and technological reasons. Considerable theoretical<sup>4</sup> and experimental<sup>5-7</sup> efforts have been therefore devoted to the study of the WF for alkali-metal-covered solid surfaces. On the other hand, understanding of the WF of sputtered surfaces is important for secondary-ion mass spectroscopy (SIMS), because the negative ion yield  $Y^-$  has an exponential dependence on the surface WF  $\phi$  (Refs. 8-11)

$$Y^- \propto \exp[-(\phi - A)/\varepsilon_0], \quad (1)$$

where  $A$  is the electron affinity of a negative ion and  $\varepsilon_0$  contains factors defining the electronic interaction with the surface. Yu<sup>10</sup> says  $\varepsilon_0$  should be proportional to the normal component of the emission velocity  $\nu$  of the negative ion, but Šroubek, Žďánský, and Zavadil, say it should be relatively independent of  $\nu$  (Ref. 12).

Determination (relative) WF has been performed by several methods<sup>13</sup> such as those utilizing a Kelvin probe, photoemission, secondary electrons,<sup>14</sup> and secondary ions.<sup>15-17</sup> The method utilizing secondary ions is based on measurement of the onset of secondary-ion energy distribution. The energy-distribution shift, which indicates the variation of the contact potential between the sample and the energy analyzer, can provide a means of *in situ* determination of WF change. By this method, the WF change can be determined to an accuracy better than 0.1 eV (Ref. 16).

It has been well known<sup>18</sup> that ion implantation results in an atomic displacement, which leads to production of damages, namely, various defects, structural modification, and surface topography change. The degree of damages depends on the implant conditions, namely, the ion energy, flux, and fluence, as well as mass and atomic number of the host and guest atoms. The degree of damage to the near-surface region affects the WF of a solid surface.<sup>7</sup>

In this paper, we determined on the depth dependence of the relative WF change of the damaged layer that is produced in Si wafers by implant with high dose <sup>11</sup>B<sup>+</sup> ions, using SIMS technique.

### II. EXPERIMENT

<sup>11</sup>B<sup>+</sup> ions were implanted into Si(100) wafers at 35 keV with a dose of  $5 \times 10^{16} \text{ cm}^{-2}$ . The wafer temperature was carefully controlled during implantation in order to prevent wafer heating due to higher dose rates.

Dynamic-mode sputtering and measurement of the WF change were performed with a Cameca IMS-4f SIMS instrument, which is equipped with a double-focusing mass spectrometer. The working pressure was  $1 \times 10^{-9}$  Torr. A Cs<sup>+</sup> primary ion beam was rastered over an area of  $150 \times 150 \mu\text{m}^2$  with an impact energy of 14.5 keV and an incident angle of 25° from the surface normal. The primary ion beam current was 5 nA, corresponding to an ion flux of  $1.4 \text{ ions/cm}^2 \text{ s}$ . Negative secondary ions from the central area of the sputtered crater were detected. When the slit of the kinetic energy filter is close to a few eV and the mass spectrometer is fixed, the selected ions are detected with a given kinetic energy, which is the total of the initial energy and extraction energy. Thus, the energy distribution can be determined by varying the extraction voltage. In this experiment, the secondary-ion energy distribution was measured by varying the sample potential in steps of 0.1 V (Ref. 19) around -4.5 kV by a computer control. The variations of the sample WF were determined by the shift of the secondary-ion energy distribution. In order to measure the relative WF change at each sputter depth, the WF measurement and the sputter erosion of sample were performed alternately. The sputtered depth was checked by the erosion rate. The amount of Cs adsorbed on the Cs<sup>+</sup> sputtered surface was measured with a Physical-Electronics PHI-660 Auger electron spectroscope (AES). The structural properties were examined with a JEOL JEM-4000fx transmission-electron microscope (TEM).

### III. RESULTS AND DISCUSSION

According to Eq. (1), the measurement of secondary-ion intensity can be used to assess the relative WF change  $\Delta\phi$  of

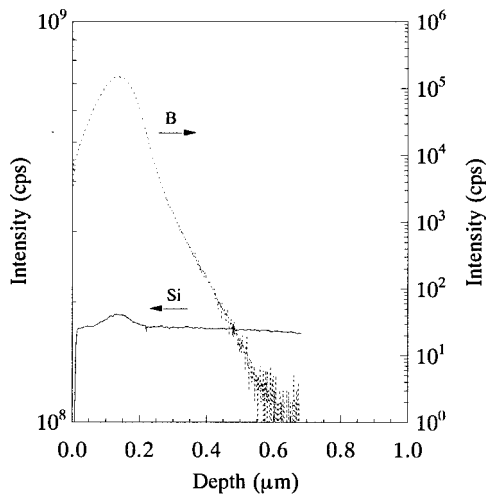


FIG. 1. SIMS depth profiles of  $^{28}\text{Si}^-$  and  $^{11}\text{B}^-$  from  $\text{B}^+$ -implanted Si wafers (35 keV,  $5 \times 10^{16} \text{ cm}^{-2}$ ).

sputtered surface. Therefore, the SIMS depth profiles of  $^{28}\text{Si}^-$  and  $^{11}\text{B}^-$  were measured, and the results are shown in Fig. 1. As already known from previous studies,<sup>20</sup> the intensity of the secondary ions increases very rapidly at the initial stage of depth profiles. This enhancement of the ion yield is due to the gradual build up of implanted Cs which causes the decrease of the WF. The relationship between the  $\text{Si}^-$  intensity and  $\Delta\phi$  is shown in Fig. 2. The  $\text{Si}^-$  intensity was recorded in the peak of the secondary-ion energy distribution. The WF decreases with the progress of sputtering, i.e., with increasing Cs coverage of the bombarded surface. No drastically increase of the  $\text{Si}^-$  intensity was observed with further decreasing of  $\Delta\phi$  beyond 2.5 eV. Similar behavior has been reported by Yu<sup>10,11</sup> in Cs-adsorption experiments. The relative stationary  $\Delta\phi$  observed when a relatively steady state of Cs coverage ( $\sim 30 \text{ nm}$  in Fig. 1) has been reached is 2.6 eV, which is smaller than that of other data ( $\sim 3.0 \text{ eV}$ ).<sup>6,7,11</sup> The reason for this difference is interpreted as follows: As soon as the WF measurement starts, Cs is adsorbed on the sputtered surface. Consequently, the initial WF is already reduced. This leads to a smaller  $\Delta\phi$  than that of Refs. 6, 7, and 11. From the slope of region (B) in Fig. 2, the value of  $\varepsilon_0$  is found to be 0.65 eV, which is larger than 0.49 eV reported by Gnaser.<sup>17</sup> The difference in the  $\varepsilon_0$  value stems

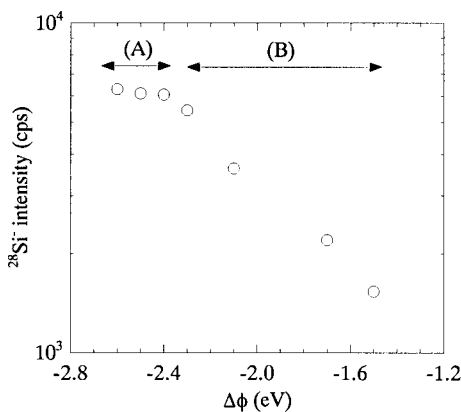


FIG. 2. Dependence of the  $\text{Si}^-$  yield on the relative work-function change.

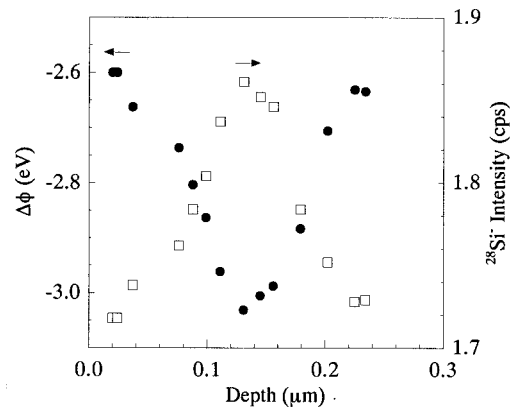


FIG. 3. Calculated values of the relative work-function change (full circles, left-hand scale) and the measured intensity of  $\text{Si}^-$  (open squares, right-hand scale) as a function of depth at the boron peak region.

probably from the emission velocity dependence of  $\varepsilon_0$ .

Another interesting aspect is that the  $\text{Si}^-$  intensity is enhanced at the peak region of the boron profile (Fig. 1). Considering the limit of experimental accuracy, except at the maximum point of the  $\text{Si}^-$  intensity, it is more difficult to measure  $\Delta\phi$  in this region. Hence,  $\Delta\phi$  has been estimated by using both parameter  $\varepsilon_0$  (5.4 eV) obtained in region (A) of Fig. 2 and the values of  $\text{Si}^-$  intensity in Fig. 1. The calculated  $\Delta\phi$  values at the boron peak region are shown in Fig. 3, which also includes the variation of  $\text{Si}^-$  intensity. The maximum  $\Delta\phi$  ( $-3.1 \text{ eV}$ ) is consistent with the experimental value (3.0 eV). The intensity of  $\text{Si}^-$  increases with decreasing WF. It was found that the enhancement of  $\text{Si}^-$  intensity (Fig. 1) is explained by the lowering of surface WF.

In order to better understand this phenomenon, we have investigated the defects created by  $^{11}\text{B}^+$ -ion implantation by cross-sectional transmission-electron microscopy (XTEM). The result is shown in Fig. 4. A completely amorphous layer and defects are formed in the direction from the surface to the substrate. Some roughness is observed at the interface between the amorphous layer and the defect region. According to a result reported previously,<sup>7</sup> the maximum coverage of Cs and the WF change are greater on a  $\text{Si}(100)2 \times 1$  with  $\text{Ar}^+$ -bombardment surface than that without bombardment,

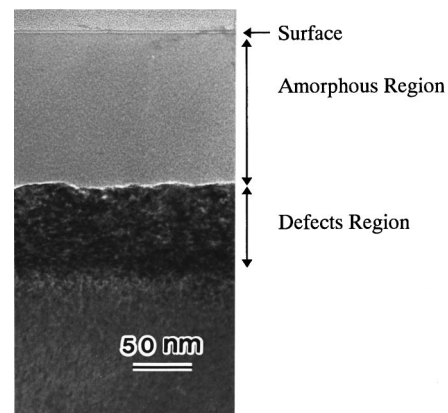


FIG. 4. Cross-sectional TEM (XTEM) image of a Si wafer implanted with 35 keV  $^{11}\text{B}^+$  at a dose of  $5 \times 10^{16} \text{ cm}^{-2}$ .

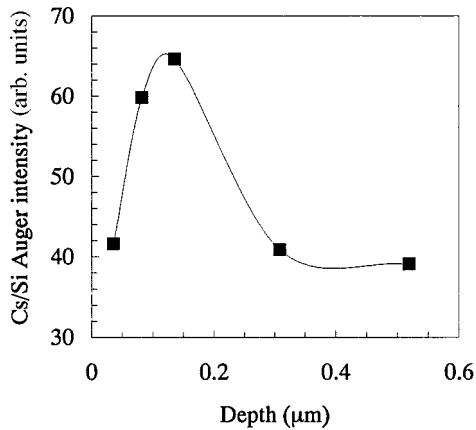


FIG. 5. Ratio of Cs(555 eV)/Si(78 eV) Auger peak-to-peak heights as a function of depth.

and this behavior is attributed to the new adsorption sites created by the presence of defects. It would be considered that a similar phenomenon exists in the present experiment.

Then, the Cs coverage was investigated by AES. Figure 5 shows the  $(Cs_{MNN}555 \text{ eV})/(Si_{LMM}78 \text{ eV})$  Auger peak-to-peak height ratio obtained at each sputter depth by  $Cs^+$  bombardment. As seen in this figure, the Cs coverage reaches a maximum at the depth of  $\sim 0.15 \mu\text{m}$  the peak region of the

boron profile. This result indicates that the variation of Cs coverage at each depth may be ascribable to the dependence of the number of Cs traps on the Si crystal structure. The magnitude of the  $Si^-$  yield, which is influenced by the WF, is dependent on the extent of Cs coverage.

#### IV. CONCLUSION

We have reported that the depth dependence of the relative WF change in  $B^+$ -implanted Si wafers. It was found that the  $Si^-$  yield, and incorporated Cs coverage reach their maximum, while the WF becomes minimum at the interface region between the completely amorphous and the defects layer, which the interface corresponds to the peak of the boron profile. These phenomena can be explained by the fact that the amount of adsorbed Cs reaches a maximum due to the increase of adsorption sites at the defects region, in particular at the interface.

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