Effect of the Flash Annealing on the Impurity Distribution and the Electronic Structure in the Inversion Layer

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We investigated the relationship among the number of flash annealing times to obtain Si clean surface and the change of arsenic dopant concentration and subband levels using secondary ion mass spectroscopy (SIMS) and angle-resolved photoelectron spectroscopy (ARPES). The SIMS result shows that the first five times of the flash annealing already induces significant reduction of the dopant concentration in agreement with the recent work [Pitter et al., J. Vac. Sci. Technol. B 30, 021806 (2012)]. We found the energies of hole subband levels rapidly decrease as the number of the flash annealing times increases. We calculated the subband levels in a broadened confinement potential taking the dopant reduction determined by SIMS into account. The energy separations of the calculated subband levels were in good agreement with the ARPES results. [DOI: 10.1380/ejssnt.2015.75]

Keywords: Angle resolved photoemission; Pb; Si(111); Hole subband; Dopant

I. INTRODUCTION

Hole subbands, quantized electronic structure confined in silicon inversion layer (IL), has been recently observed by ARPES in the system of In/Si(111) [1, 2], Pb/Si(111) [3], PbGa/Si(111) [4] and Pb/Si(001) [5]. The subband dispersion structures were clearly detected in these works. Subband energy levels at the gamma point are compared with the theoretical values obtained by triangular potential approximation (TPA). Though the measured energy levels were in good agreement with the theoretical values in most cases, significant deviation was observed in some cases [2, 4, 5]. In the case of Pb/Si(001) [5], the origin of the deviation was speculated to be the reduction of dopant concentration caused by dopant out-diffusion during flash annealing process [6], which is a conventional method to make a clean silicon surface. Because the reduction of dopant concentration leads to increase of the width of inversion layer, dopant concentration is crucial to the subband energy levels confined in IL. Dopant diffusion in Si subsurface region has been studied in detail for several decades especially in terms of the process of MOSFET fabrication [7–9]. However, the effect of flash annealing in UHV on the dopant concentration has been still under discussions [10, 11]. In this article, we examined the validity of the above speculation quantitatively by investigating the relationship between the subband energy separation and the dopant concentration using ARPES and SIMS.

II. EXPERIMENTAL

A heavily arsenic (As)-doped Si(111) wafer was used. The impurity concentration was $3.5 \times 10^{19}$ (atoms/cm$^3$). Each sample was cleaned by flash annealing at 1250°C ($\geq 1$ sec) using direct heating method in UHV [12]. The temperature of these samples were raised up to 1250°C within 2 sec from RT and decreased to RT as soon as reaching 1250°C during flash annealing. In this study, the number of the flash annealing of each sample were strictly controlled so as to see the effect of the flash annealing on the subband energy. We prepared 9 samples with different number of the flash annealing times which are 0 time, 1 time, 5 times, 20 times, 40 times, 70 times, 100 times, 250 times and 300 times. After confirming the Si(111)$7 \times 7$ clean surface by RHEED, Pb was deposited on the clean surface for a few ML at RT. Then, the sample was annealed at 300°C for a few minutes and we confirmed Si(111)$\sqrt{3} \times \sqrt{3}$-Pb SiC structure [13]. The band structure of these samples were measured by ARPES with He discharge lamp (21.2 eV) in UHV [12]. After the ARPES measurement, 5 samples (flash annealed for 0, 1, 5, 100, and 300 times) were extracted to the air and loaded to SIMS chamber to measure dopant distribution. SIMS measurement was performed with Cs ion beam of 1 keV to detect the dopant (As) in the Si substrate.

III. RESULTS AND DISCUSSION

The hole subband structures from the sample flash annealed for 300 times and the photoelectron spectra at $\Gamma$ point with various flash annealing times are shown in

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Dopant concentration (cm\(^{-3}\))

Depth from the surface (nm)

- no flash annealing
- 1 time
- 5 times
- 100 times
- 300 times

FIG. 2. Impurity (Arsenic) distribution measured by SIMS which depends on flash annealing times. The etching rate was 0.1 (nm/sec) with Cs\(^+\) 1 keV.

Fig. 1 (a) and (b), respectively. These subband structures were measured along [11\(_2\)] direction. The subband energy levels, E\(_0\), E\(_1\), and E\(_2\), appeared in the all samples at Γ point (1 time-300 times). All energy levels were determined by Voight fitting. There is a systematic energy shift of peaks E\(_0\), E\(_1\), E\(_2\) depending on the number of flash annealing times. We will discuss the dependency later together with the result of SIMS. The distribution of impurity concentration in the samples which were flash annealed for 1, 5, 100, 300 times and not flash-annealed are investigated by SIMS as shown in Fig. 2. The dopant in no flash-annealed sample is uniformly distributed from the surface to the bulk. On the other hand, the dopant concentration in the flash annealed sample decreases in the region between the surface and 50 nm. The SIMS results indicate that flash annealing have considerable effect on the impurity distribution curve in the subsurface region. In order to estimate the amount of the reduction of the impurity at subsurface region quantitatively, the relative areal density (RAD) of the impurity which shows in Eq. (1) was introduced.

\[
\text{RAD} = \frac{\int_0^x C(x,t)dx}{\int_0^x C(x,0)dx}, \quad (1)
\]

Here, \(x\) is the depth from the surface and \(t\) is the time which the sample was at maximum temperature for, respectively. \(C(x,t)\) is the dopant distribution. Hence, the denominator of Eq. (1) indicates the areal density of the dopant in as-shipped wafer. In Fig. 3, the subband energy levels, E\(_0\), E\(_1\), and E\(_2\), defined from Fig. 1 and the RAD within 50 nm from the surface (\(x = 50\) nm) derived from Fig. 2 are plotted against the number of flash annealing time. In the region between 0 times and 5 times (region I), the RAD decreased rapidly. The energy levels (E\(_0\), E\(_1\)) shift toward lower binding energy significantly in this region. The energy shifts of E\(_0\) and E\(_1\) from 0 times to 5 times were 0.19 eV and 0.26 eV respectively, as shown in Fig. 3(a). The energy separation between E\(_0\) and E\(_1\) decreases by 20%. The decrease of the RAD makes the slope of the band bend shape gentle. Thus, energy levels shifted toward low binding energies and the energy separations decreased. In the region between 5 times and 100 times (region II), the slight reduction of the RAD was observed. Energy levels E\(_0\), E\(_1\) and E\(_2\) also slightly shifted to lower binding energy by 0.03 eV, 0.04 eV and 0.09 eV, respectively, as shown in Fig. 3(a). Energy separations (E\(_0\)-E\(_1\), E\(_1\)-E\(_2\)) show a reduction of 5 % and 13 %, respectively. In the region between 100 times and 300 times (region III), the RAD was nearly constant. And the energy shift was not observed. Similarly, energy separations were unchanged as shown in Fig. 3(b). This result indicates that the energy levels which locate in higher binding energy were strongly influenced by the decreasing the impurity concentration at subsurface region and significant energy shifts occur. As a result, energy separation was decreased by the reduction of the RAD. Therefore, the dopant concentration which depend on flash annealing times correlates with subband energy level and energy separation. Especially, the RAD of the dopant is remarkably decreased at the region I (less than 5 times). It makes the subband structure change dramatically. We calculated the band bending and the subband energy separations by considering the decreasing of the dopant in the subsurface region of the sample flash annealing for 300 times. The band bending curve was obtained as the solution of Poisson equation which includes in Debye length [14]. The dopant concentration in the subsurface region of the sample with 300 times flash annealing, 7.0 × 10\(^{18}\) (cm\(^{-3}\)), was determined by averaging the concentration obtained by the SIMS in the region to 20 nm from the surface. The valence band maximum at the surface (denoted as V\(_0\)) is obtained by V\(_0\) = VBM\(_{\text{Si}(111)7\times 7}\) − \(\Delta V_{3d\text{P}}\). Here, VBM\(_{\text{Si}(111)7\times 7}\) is known to be 0.63 eV [15]. \(\Delta V_{3d\text{P}}\) is the shift of the valence band maximum at the surface between Si(111)\(_7\) \(\times\) 7 and Si(111)\(_7\)\(\sqrt{3}\) \(\times\) \(\sqrt{3}\)-Pb. It is evaluated using the Si 3p peak shift [3] and obtained to be 0.54 eV in this work. Comparison of the band bending between the samples before flash annealing and after flash annealing (flash annealing times; 300 times) was shown in Fig. 4. In Fig. 4, FWHM widths of the space charge layers are roughly estimated to be 7 nm and 3 nm for 7.0 \times 10\(^{18}\) (cm\(^{-3}\)) and 3.5 \times 10\(^{19}\) (cm\(^{-3}\)), respectively. The confined width which subband energy separations depend on becomes 2.3 times wider than it obtained by the original dopant concentration. In order to calculate the subband energy levels, we
used TPA calculation [16]. \(n\)th energy levels, \(E_n\), using TPA is obtained by

\[
E_n = \left( \frac{h^2}{2m_z} \right)^{1/3} \left( \frac{3\pi eF}{2} \right)^{2/3} \left( n + \frac{3}{4} \right)^{2/3} + V_0,
\]

where \(h\) is the Plank constant, \(m_z\) is an electron effective mass along with [111] direction, \(eF\) is the slope of the energy potential obtained by the band bending (as shown in Fig. 4). The calculated results with and without considering the reduction of the impurity are compared in Table I.

Before flash annealing, the energy separations between \(E_0'\) and \(E_1'\), and \(E_1'\) and \(E_2'\) obtained by TPA show 0.32 eV and 0.54 eV as shown in Table I. On the other hand, the experimental separations obtained by ARPES are 0.18 eV (\(E_0'-E_1'\)) and 0.27 eV (\(E_1'-E_2'\)). Thus, without considering the decrease of the dopant, these subband energy separations are almost 2 times wider than the experimental one because of the narrow width of the space charge layers. The calculated energy separations between \(E_0'\), \(E_1'\), and \(E_1'-E_2'\) after flash annealing were 0.18 eV, 0.30 eV, respectively as shown in Table I. Unlike the calculated energy separations before flash annealing, the subband energy separations after flash annealing by TPA are in good agreement with the experimental one. The energy separations of the subband obtained by ARPES show the narrower than the energy separations with the original dopant.

IV. CONCLUSION

In summary, we demonstrated that the dopant concentration and the energy level separation of hole subbands decreases by flash annealing. The SIMS result shows the dopant concentration within 50 nm from the surface significantly decreases with the flash annealing only for 5 times. The dopant concentration almost saturated with the flash annealing for more than 100 times. The subband levels show similar behavior on the number of the flash annealing times. In the flash annealed sample, the confinement potential for subbands broadens due to the expansion of the width of the space charge layers caused by the reduction of the dopant concentration in the subsurface region. We quantitatively examined the effect of the reduction of dopant concentration on the subbands by calculating the subband levels in the broadened confinement potential. The calculated result shows in good agreement with the ARPES results. This ensure that the speculation in the former study is valid, which means that the reason of the narrower energy separation of the subbands is due to the reduction of the dopant concentration brought by the flash annealing. This results mean that the subband energy separations are sensitive to the change of the dopant distribution within subsurface. We should consider the considerable effect of the flash annealing on the dopant distribution.

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