Fermi level pinning on Si 0.83 Ge 0.17 surface by inductively coupled plasma treatment

lee-Gon Kim, Kyoung Jin Choi, and Jong-Lam Lee

Citation: *Journal of Vacuum Science & Technology B* **23**, 495 (2005); doi: 10.1116/1.1868652

View online: <http://dx.doi.org/10.1116/1.1868652>

View Table of Contents: <http://scitation.aip.org/content/avs/journal/jvstb/23/2?ver=pdfcov>

Published by the AVS: Science & Technology of Materials, Interfaces, and Processing

Articles you may be interested in

Fermi level pinning-free interface at metals/homoepitaxial diamond (111) films after oxidation treatments
Appl. Phys. Lett. **92**, 112112 (2008); 10.1063/1.2892658

Mechanism for the increase of indium-tin-oxide work function by O₂ inductively coupled plasma treatment
J. Appl. Phys. **95**, 586 (2004); 10.1063/1.1633351

X-ray photoemission spectroscopic investigation of surface treatments, metal deposition, and electron accumulation on InN
Appl. Phys. Lett. **82**, 3254 (2003); 10.1063/1.1573351

Room-temperature Ohmic contact on n-type GaN with surface treatment using Cl₂ inductively coupled plasma
Appl. Phys. Lett. **78**, 2015 (2001); 10.1063/1.1360784

Effects of helicon-wave excited N₂ plasma treatment on Fermi-level pinning in GaAs
J. Appl. Phys. **85**, 3234 (1999); 10.1063/1.369665

A PASSION FOR PERFECTION

PFEIFFER VACUUM

HiPace® M magnetically levitated turbopumps

- Simple installation
- Long service life
- Innovative bearing system

Are you looking for a perfect vacuum solution?
Please contact us!

Fermi level pinning on $\text{Si}_{0.83}\text{Ge}_{0.17}$ surface by inductively coupled plasma treatment

lee-Gon Kim, Kyoung Jin Choi, and Jong-Lam Lee^{a)}

Department of Materials Science and Engineering, Pohang University of Science and Technology, Pohang, Kyungbuk 790-784, Korea

(Received 10 September 2004; accepted 10 January 2005; published 17 March 2005)

Effects of inductively coupled plasma (ICP) treatment on Fermi level pinning on the surface of $\text{Si}_{0.83}\text{Ge}_{0.17}$ was studied by current-voltage and x-ray photoemission spectroscopy measurements. ICP treatment induced the growth of silicon oxide, suggesting that Si vacancies are generated under the oxide. From linear fitting of Schottky barrier heights with metal work functions, it was found that surface state density increased from 6.60×10^{12} to $1.13 \times 10^{13}/\text{cm}^2 \text{ eV}$ by the ICP treatment, leading to the pinning of surface Fermi level about $E_C \sim 0.53 \text{ eV}$. From this, it is suggested that the Si vacancies are the main surface states in pinning Fermi level on the ICP-treated surface. © 2005 American Vacuum Society. [DOI: 10.1116/1.1868652]

I. INTRODUCTION

Recently, silicon germanium ($\text{Si}_{1-x}\text{Ge}_x$) alloys have received considerable attention due to their tunable band gap, enhanced carrier mobility, improved high frequency behavior, and ease of integration with existing silicon technology. Several device structures have already been demonstrated, including the heterojunction bipolar transistor using a SiGe base layer¹ and optoelectronic devices² and solar cells.

Dry etching is one of the basic steps in the fabrication of SiGe-based devices, because it could transfer a fine pattern with high anisotropy. However, dry etching was known to cause ion-induced damages at the surface and near-surface region. The etch rate of $\text{Si}_{1-x}\text{Ge}_x$ alloys ($x < 0.2$) increases with the inductive power. The etch rate is enhanced compared to that of Si and the stoichiometry is changed at the surface, e.g., Si and Ge enhancement. The ion-induced damage in SiGe epitaxial layers on Si substrates were attributed to the formation of a non-stoichiometric surface due to preferential loss of one of the elements, resulting in the degradation of crystallinity of SiGe films.³ Another possible origin for the degradation is the generation of trapping centers on the etched surface.⁴ Inductively coupled plasma (ICP) etching of GaN led to severe degradation of the Schottky contact, the decrease of Schottky barrier height and the increase of the reverse leakage current by several orders of magnitudes.⁵

The Schottky barrier height (ϕ_B) of a metal/semiconductor contact is ideally determined by the difference between the metal work function (ϕ_m) and the electron affinity of the semiconductor. However, in most practical metal/semiconductor contacts, ϕ_B is determined by ϕ_m and the surface states.⁶ Since dry-etching-induced deep levels are localized near the surface of semiconductors, such deep levels could play a critical role in determining the Schottky barrier height via Fermi level pinning. However, no research has been conducted on the Fermi level pinning on the surface of fully strained $n\text{-Si}_{0.83}\text{Ge}_{0.17}$.

In this work, Fermi level pinning induced by ICP treatment was studied on the surface of fully strained $n\text{-Si}_{0.83}\text{Ge}_{0.17}$. The dependence of ϕ_B on ϕ_m was examined by current-voltage (I - V) measurements. Changes in chemical composition and surface band bending were investigated using synchrotron radiation photoemission spectroscopy (SRPES). From these, the origin for the ICP-induced surface states was suggested.

II. EXPERIMENT

The n -type SiGe sample used in this study was a fully strained 100-nm-thick epitaxial layer grown by chemical vapor deposition on a 5 in. n -type Si (001) substrate ($\rho = 3\text{--}3.5 \Omega \text{ cm}$). The film was doped *in situ* with phosphorus to a concentration of $1 \times 10^{17} \text{ cm}^{-3}$. The composition of Ge was determined to be about 17 at. % by Rutherford backscattering spectroscopy.

For the formation of Ohmic contacts on the n -type SiGe, Al (300 nm) was deposited on the backside of the sample, followed by rapid thermal annealing in an N_2 ambient at 400°C . Prior to the formation of Schottky contacts, the surface of the SiGe was treated using Ar and N_2 ICP for 1 min, respectively. During ICP etching, the inductive source power and the rf chuck power were respectively maintained 600 and 100 W at a base pressure of 5×10^{-5} Torr. No distinct change in etch depth was found in such ICP condition. Schottky diodes with a dimension of $100 \times 100 \mu\text{m}^2$ were patterned on the samples using image-reversal photolithography. The patterned samples were dipped into HF to remove the native oxides, possibly formed during the ICP treatment. Then 50-nm-thick Cr, Ru, Au, Ir, and Pt Schottky metals were deposited by electron-beam evaporation.

The changes of chemical composition and band bending at the surface of SiGe with the type of surface treatments, namely, HF treatment, ICP treatment, and ICP+HF treatment, were characterized using SRPES measurements at the 4B1 beam line of the Pohang Accelerator Laboratory. The incident photon energy was calibrated using the core level spectrum of Au 4f, used to determine the exact position of

^{a)} Author to whom correspondence should be addressed; electronic mail: jlllee@postech.edu

TABLE I. Schottky barrier height (ϕ_B) and ideality factor (η) for both HF-treated and ICP-treated samples.

Metals	HF		N ₂ ICP+HF		Ar ICP+HF	
	ϕ_B	η	ϕ_B	η	ϕ_B	η
Cr	0.464	1.57	0.436	1.50	0.420	1.43
Ru	0.512	1.76	0.488	1.71	0.476	1.42
Au	0.564	1.50	0.540	1.51	0.496	1.34
Ir	0.616	1.66	0.568	1.39	0.544	1.17
Pt	0.620	1.40	0.596	1.37	0.532	1.18

E_F at the treated surface. Also, depth information of the atomic compositions was obtained by changing the takeoff angle θ angle between the SiGe surface and the trajectory of the emitted electrons. The smaller the θ , the larger the concentration of the photoelectrons from the near surface region because of the geometrical enhancement.

III. RESULTS AND DISCUSSION

The ϕ_B and ideality factor (η) of Schottky contacts on SiGe surfaces were extracted by fitting forward I - V curves to the thermionic emission model, summarized in Table I. Figure 1 shows the change of ϕ_B as a function of ϕ_m . ICP treatment resulted in the decrease of ϕ_B as well as the slope in the plot of ϕ_B versus ϕ_m . The dependence of ϕ_B on ϕ_m was determined, respectively, to be $\phi_B=0.16 \cdot \phi_m - 0.252$ for the HF-treated sample, $\phi_B=0.13 \cdot \phi_m - 0.127$ for the N₂ ICP-treated one, and $\phi_B=0.10 \cdot \phi_m + 0.02$ for the Ar ICP-treated one. The absolute value of the slope was decreased from 0.16 to 0.13 for the N₂ ICP-treated sample and to 0.10 for the Ar ICP-treated one. This means that ICP treatment created surface states at which the surface Fermi level (E_F) is pinned more strongly.

FIG. 1. Schottky barrier height of Cr, Ru, Au, Ir, and Pt contacts on n -Si_{0.83}Ge_{0.17} with metal work function before and after N₂ and Ar ICP treatments.

TABLE II. Change of slope parameter (S), surface state density (D_s), and the surface Fermi energy (ϕ_0) of n -type SiGe with the type of surface treatment.

	S	a	D_s (cm ⁻² eV ⁻¹)	ϕ_0 (eV)
HF	0.16	-0.252	6.62×10^{12}	0.56
N ₂ ICP+HF	0.13	-0.127	8.41×10^{12}	0.53
Ar ICP+HF	0.10	0.012	1.13×10^{13}	0.52

One can determine the density of surface states D_s causing the band bending below the surface. The relationship of ϕ_B with ϕ_m is expressed in Eq. (1)⁶

$$\phi_B = S(\phi_m - \chi_s) + (1 - S) \left(\frac{E_g}{q} - \phi_0 \right) - \Delta\phi \equiv S\phi_m + a, \quad (1)$$

where E_g is band gap ϕ_0 , E_F at the surface, $\Delta\phi$ the barrier height lowering by image force, S the slope in the plot of ϕ_B with ϕ_m , χ_s the electron affinity, and a is a constant. Therefore ϕ_0 can be calculated using Eq. (1) and D_s can be determined using $D_s = [(1 - S)\epsilon_i] / S\delta q^2$. Here, ϵ_i is the permittivity and δ is the thickness of interfacial layer between metal and semiconductor. By linearly fitting data in Fig. 1 with Eq. (1) using $\chi_s = 4.05$ eV⁷ and $\delta = 44$ Å,⁸ the values of S , a , ϕ_0 , and D_s were determined, summarized in Table II. For the HF-treated sample, D_s was determined to be 6.60×10^{12} cm⁻² eV⁻¹, but it increased to 8.41×10^{12} and 1.13×10^{13} cm⁻² eV⁻¹ after N₂ and Ar ICP treatment, respectively. Due to the increase in D_s after ICP treatment, surface E_F was found to be pinned at ~ 0.53 eV from the conduction band edge.

Figure 2 shows the evolution of the Si 2p and Ge 3d XPS spectra with the step of surface modifications such as HF, Ar ICP, and Ar ICP+HF treatments. Incident photon energy of 610 eV was used for measurement of the core-level spectra of Si 2p and Ge 3d. The takeoff angle for all spectra was 90°. Si 2p and Ge 3d spectra were separated into two component peaks, originated from spin-orbit coupling. In the Si 2p spectrum of the as-grown sample, a peak corresponding to

FIG. 2. Si 2p and Ge 3d XPS spectra before and after various surface modifications using HF, Ar ICP, and Ar ICP+HF treatments.

FIG. 3. Photoemission onset of secondary electrons with the type of surface treatment.

oxidized Si was observed at the binding energy of 102.6 eV. The oxide peak disappeared by HF etching, but appeared again after the ICP treatment. It was found that a peak corresponding to Ge oxide appeared at 32.2 eV. From this, it was suggested that the ICP-induced oxide layer is primarily composed of Si oxide with a small amount of Ge oxide. The Gibbs free energy change for the formation of each oxide is as follows: namely, $-\Delta G(700^\circ\text{C})$ in the reaction of $\text{Si} + 2\text{O}_2 \rightarrow \text{SiO}_2$ is 728.9 kJ/mol,⁹ which is larger than 482.3 kJ/mol of $\text{Ge} + 2\text{O}_2 \rightarrow \text{GeO}_2$.¹⁰ Thus, the surface became Si deficient as the ICP-induced oxides were removed through the HF etching.

There was no change in the full width at half maximum, but the binding energies of Si 2*p* and Ge 3*d* spectra changed with the type of surface treatment. The peak shifts after HF and (ICP+HF) treatments are related to the removal of the as-grown and ICP-induced oxide layers. It is also worth noting the changes in the peak positions between the HF- and (ICP+HF)-treated samples, because Schottky diodes in Fig. 1 were fabricated on both surfaces. The binding energies of Si 2*p* and Ge 3*d* spectra were moved to higher energy by 0.15 and 0.21 eV after (ICP+HF) treatment, respectively. This means that E_F at the surface of SiGe moved about 0.18 eV on average near the conduction band edge by the ICP treatment, leading to a decrease of the effective ϕ_B for the transport of electrons, consistent with the result of Fig. 1.

Figure 3 shows photoemission onsets of secondary electrons with the step of surface treatment. The relative change of χ_s can be determined from a sharp photoemission onset of the secondary electrons. The onset energies of the as-grown and ICP-treated samples were nearly the same, because chemical composition and bonding states on both surfaces are similar to each other, because of the presence of oxide layers on the surface. The kinetic energy shifted towards higher energy levels after HF cleaning. This is due to the disappearance of oxide layer with low χ_s . The kinetic energy in the (ICP+HF)-treated sample was higher than that in the HF-treated one. From this, it is proposed that the ICP treatment of SiGe produces the Ge-rich surface in Fig. 2 and the χ_s increased with ICP treatment.

The atomic percentages of XPS peaks or Si 2*p* and Ge 3*d* core level spectra were determined using the peak area and

FIG. 4. Ratios of Si/Ge with takeoff angle before and after ICP treatment. Peak intensities were obtained by integrating each peak area.

the atomic sensitivity factor of each element. Using the atomic percentage of each element, the ratios of Si/Ge with the detection angle θ were determined, as shown in Fig. 4. The value of the Si/Ge ratio at the normal detection ($\theta=90^\circ$) of (ICP+HF)-treated sample was set as 1.0 for reference. The Si/Ge ratio of the (ICP+HF)-treated sample is lower than that of the HF-treated one and the ratio decreased at a lower detection angle. The decrease in the Si/Ge ratio at the smaller angle after the ICP treatment and the subsequent HF cleaning is indicative of the formation of a Si-deficient layer near the surface due to the generation of Si vacancies. In moderately and highly doped *n*-type Si, a dominating defect was observed after irradiation by high energy particles, identified as a vacancy–donor complex.¹¹ The thermal activation energy of this complex was reported to be dependent on both the type of donors and Ge content in strained epitaxial $\text{Si}_{1-x}\text{Ge}_x$. In phosphorus-doped Si and $\text{Si}_{1-x}\text{Ge}_x$, for instance, the vacancy–phosphorus level exhibited a nonlinear dependency on Ge content with a sharp increase of the thermal activation energy at $x=0.04$ and the level was saturated at 0.53 eV for higher Ge content.¹² The saturated vacancy–phosphorus level agrees well with E_F pinning position at the

FIG. 5. Energy band diagrams of the HF- and (ICP+HF)-treated surfaces constructed based upon the change in electron affinity by ICP etching, as in Fig. 3.

surface of $\text{Si}_{0.83}\text{Ge}_{0.17}$ as shown in Table II. From this, it is suggested that Si vacancy-related surface states pin surface E_F , which in turn lower ϕ_B .

Figures 5(a) and 5(b) show the schematic energy band diagrams of the HF-treated and (ICP+HF)-treated surfaces, respectively, based upon the SRPES results in Figs. 3 and 4. As the ICP-treated sample was treated with the HF solution, a number of vacancy-related surface states were exposed to the surface. The binding energy was increased by 0.18 eV on average in Fig. 2, meaning the decrease of SBH by the ICP treatment, due to the generation of vacancy-related surface states, as shown in Fig. 5(b). The relative increment in the χ_s of (ICP+HF)-treated sample was 0.23 eV as shown in Fig. 3. As a result, Fermi level shifts towards CBM, resulting in the decrease of SBH via the smaller surface band bending, as shown in Fig. 4(b).

IV. CONCLUSION

ICP treatment resulted in the decrease of ϕ_B . By linearly fitting the relation between ϕ_B and ϕ_m , D_s was determined to be $6.60 \times 10^{12} \text{ cm}^{-2} \text{ eV}^{-1}$ for the HF-treated sample, but it increased to 8.41×10^{12} and $1.13 \times 10^{13} \text{ cm}^{-2} \text{ eV}^{-1}$ after N_2 and Ar ICP treatment, respectively. The increase in D_s resulted in pinning of surface E_F at $E_C \sim 0.53 \text{ eV}$. The increase of binding energies of both Si 2*p* and Ge 3*d* peaks by the ICP treatment means the movement of surface E_F near the conduction band edge. The peak intensities of Si 2*p* and Ge 3*d* increased by the ICP, but the increase of Si 2*p* peak was more pronounced. This means that the production of Si oxide is more dominant than that of Ge oxide. The preferen-

tial oxidation of Si caused the generation of Si vacancies, playing a role in pinning E_F at the surface of $\text{Si}_{0.83}\text{Ge}_{0.17}$ and in turn lowered lower ϕ_B .

ACKNOWLEDGMENTS

This work was performed through the project for “National Research Laboratory” sponsored by the Korea Institute of Science and Technology Evaluation and Planning (KISTEP). SRPES experiments were carried out at 4B1 beam line in Pohang Accelerator Laboratory (PAL).

- ¹Z. Q. Ma, S. Mohammadi, P. Bhattacharya, L. P. B. Katehi, S. A. Alterovitz, and G. E. Ponchak, *IEEE Trans. Microwave Theory Tech.* **50**, 1101 (2002).
- ²Z. Pei, C. S. Liang, L. S. Lai, Y. T. Tseng, Y. M. Hsu, P. S. Chen, S. C. Lu, M.-J. Tsai, and C. W. Liu, *IEEE Electron Device Lett.* **24**, 643 (2003).
- ³J. Chen, K. M. Tan, N. Wu, W. J. Yoo, and S. H. D. Chan, *J. Vac. Sci. Technol. A* **21**, 1210 (2003).
- ⁴S. C. Ahn, S. Y. Han, J.-L. Lee, J. H. Moon, and B. T. Lee, *Met. Mater. Int.* **10**, 103 (2004).
- ⁵X. A. Cao *et al.*, *Appl. Phys. Lett.* **75**, 232 (1999).
- ⁶S. M. Sze, *Physics of Semiconductor Devices*, 2nd ed. (Wiley, New York, 1981), pp. 270–278.
- ⁷D. J. Robbins, L. T. Canham, S. J. Barnett, A. D. Pitt, and P. Calcott, *J. Appl. Phys.* **71**, 1407 (1992).
- ⁸V. Craciun, E. S. Lambers, R. K. Singh, and I. W. Boyd, *Appl. Surf. Sci.* **186**, 237 (2002).
- ⁹J. M. Madsen, Z. J. Cu, and C. G. Takoudis, *J. Appl. Phys.* **87**, 2046 (2000).
- ¹⁰V. Craciun, I. W. Boyd, B. Hutton, and D. Williams, *Appl. Phys. Lett.* **75**, 1261 (1999).
- ¹¹S.-L. Sihto, J. Slotte, J. Lento, K. Saarinen, E. V. Monakhov, A. Yu. Kuznetsov, and B. G. Svensson, *Phys. Rev. B* **68**, 115307 (2003).
- ¹²E. V. Monakhov, A. Yu. Kuznetsov, and B. G. Svensson, *Phys. Rev. B* **63**, 245322 (2001).