(7×7) reconstruction as barrier for Schottky-barrier formation at the Ga/Si(111) interface

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We report the change in electronic properties of the Ga/Si interface by monitoring the Ga(3*d*) core-level photoelectron spectra and electron diffraction induced by submonolayer Ga adsorption on Si(111)-7×7 surface. The spectra shows a flat band for submonolayer coverages, attributed to the metallic nature of the Si(111)-7×7 reconstruction and a premetallic band structure of two-dimensional Ga islands. At 1 ML, electron diffraction pattern shows metallic (7×7) to semiconducting (1×1) phase-transition and the spin-orbit split branching ratio of Ga(2*p*) core level attain the metallic bulk value, and the barrier assumes the Schottky–Mott value while full width half maxima and branching ratio attain bulk values.
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Motivated by the need to form high performance devices such as Schottky devices, δ-doping, etc., the Schottky barrier problem has engaged researchers for a long time. Frequently observations are being revealed to understand the metal-semiconductor interface precisely at the atomic scale with the metal/Si surface as model systems.[1] Though the enigmatic Si(111) (7×7) reconstruction is the most stable and the most intensely studied surface, a consensus on the actual atomic arrangement of this selvedge was arrived at after intense research, as Dimer–Adatom–Stacking (DAS) fault model.[2] This DAS model consists of 108 atoms per unit cell and shows a quasicontinuous distribution of states within the bulk band gap of Si. The interesting fact of relevance to this study, is that some surface states lying close to the Fermi level disperse near the zone boundary cross the Fermi-level, resulting in a metallic character of the Si(111)-7×7 reconstructed surface.[3] Adsorption of metals on this complicated reconstruction has offered great challenges and also opportunities to utilize its diversity for tailoring properties of devices.[4]

Since it was shown that a single monolayer of group III metal on silicon surface can pull the surface Fermi level above the conduction band, resulting in degenerate doping, several surface science studies have probed this interface.[5] Most studies to date have concentrated on the adsorption of Ga on Si substrates held at high temperatures,[6] while those on the initial stages of the Ga/Si interface formation at RT have been almost negligible, due to the perception of lack of superstructural phases.[7] We have earlier reported several results of surface phases and superstructures formed of metal on Si surfaces.[8–10] Here, we revisit the evolution of the Ga/Si(111) 7×7 at room temperature. Using *in situ* X-ray Photoelectron Spectroscopy (XPS), Auger electron spectroscopy (AES), and low energy electron diffraction (LEED), we show that for low Ga coverages, the (7×7) phase and act smallness of two-dimensional (2D) islands barrier to the band bending and Schottky barrier formation.

The experiments including adsorption and analysis, were performed *in situ* in an ultra high vacuum (UHV) chamber with a base pressure of 3×10^{-11} torr. The sample was cleaned by a modified Shiraki process[11] to remove the hydrocarbons and form a thin SiO_2 epilayer before being introduced into the UHV chamber. *In situ*, the sample was heated by a combination of radiative, resistive, and electron bombardment heating to carefully cover the entire temperature range of 300–1500 K. A W–Re 5%–25% thermocouple and an optical pyrometer were used to monitor the temperature. The sample was annealed at 1100 K for several hours and flashed to 1400 K and slowly cooled, to result in an atomically clean surface with impurity levels below the detection limit of XPS, and a well ordered (7×7) LEED pattern. Ga was adsorbed from a homemade Ta Knudsen cell, with a steady beam flux. The adsorption process was monitored by an x-ray photoelectron spectrometer with a hemispherical sector electron energy analyzer (Phi Make 279.4 mm diameter with 25 meV resolution) and a Mg K_α (1253.6 eV) source. A Varian four-grid optics was used to probe the surface structure by LEED and a cylindrical mirror analyzer (0.18% resolution) with a concentric electron gun, for EELS studies.

Figure 1 shows the Ga uptake curve at room temperature, which is a plot of the XPS core level intensity ratio of the adsorbate (Ga_{3d}) and substrate (Si_{2p}) as a function of time of adsorption, and enables us to follow the adsorption kinetics.[8] The graph shows a linear increase in the Ga/Si ratio up to about 30 min and then a change in the slope, since the secondary electrons originating from the first layer are attenuated by the second adatom layer. The ratio saturates after 60 min of Ga adsorption. This is characteristic of the Stranski–Krastnov (two layers plus islands) growth mode (Shown as schematic in the figure). We also plot (dotted curve) the sum of squares of errors (SSQ) in the least-square fits of a set of two straight lines near the change in slope, whose minima identifies the inflexion point, which has previously been identified as coverage of 1 ML.[12] This gives us the calibration of the Ga flux as 0.03 ML/min.

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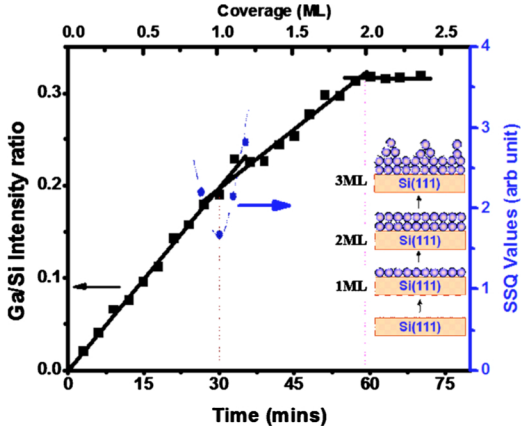

FIG. 1. (Color online) Uptake curve of the Ga($3d_{5/2}$)/Si($2p$) intensity ratio as a function of Ga deposition time. Also shown by the dotted curve (alternate Y-axis) is the SSQ to determine the 1.0 ML break at 30 min. Inset shows the schematic of the Stranski–Krastnov growth mechanism.

Figure 2 shows the coverage dependent evolution of the Ga $3d$ core level spectra, with the change in peak position and full width half maxima (FWHM) plotted on alternate axes. Curve 2(a) shows the positions of the Ga $3d_{5/2}$ peak as a function of Ga coverage. The peak at 18.2 eV remains almost unchanged (less than 0.1 eV) up to coverage of 1 ML and then sharply shifts to 19.0 eV within 5 min of adsorption, showing a shift of 0.8 eV. After 1 ML, the peak position shifts monotonically toward lower binding energy by 0.2 eV at Ga coverage of 2.3 ML. Shifts in the core level peak position in metal-semiconductor interfaces are generally attributed either to formation of Schottky barrier due to band-bending at the substrate surface or to a chemical interaction between the adsorbate and the substrate.[13] The chemical interaction is highly unlikely at these temperatures for this system as a sharp interface is an established fact. Usually the Schottky barrier increases continuously with increasing metal coverage up to a saturation value. Thus, it is interesting that in our case the Ga $3d$ core level peaks do not undergo any shift in the submonolayer regime while at about 1 ML there is a sharp shift by about 0.8 eV. Figure 2 shows, after attaining a value of 19.0 eV in the Ga $3d$ peak shift, the

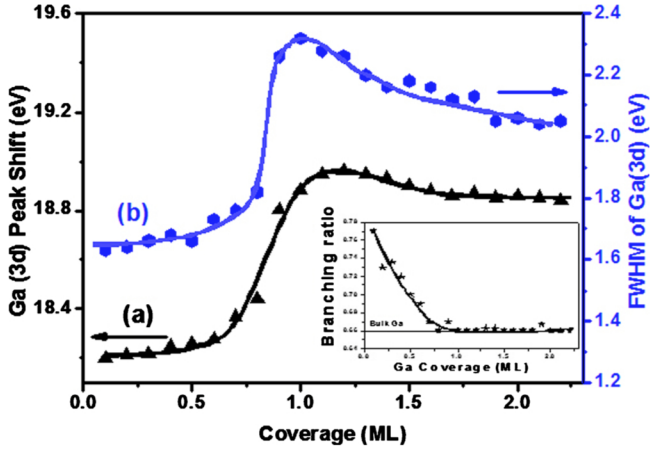

FIG. 2. (Color online) (a) Plot of Ga $3d$ peak position as a function of Ga coverage at RT. (b) Shows dependence of the FWHM of Ga $3d$ peak on Ga coverage at RT. Inset in the figure shows the change in branching ratio of the intensities of the Ga($2p_{1/2}$) and Ga($2p_{3/2}$) spin orbit split levels as a function of the Ga adsorption time and coverage.

barrier decreases to a value about 18.8eV as the coverage increases to 2.3ML attaining the Schottky–Mott value of barrier height of 0.6 eV for Ga/Si interface.[14] The presence of interface states at lower coverages shifts the charge neutrality level φ_0 below E_f, thus the width of the depletion region and barrier height φ_b will be increased pulling φ_0 up toward E_f. Therefore, the presence of interfacial states for submonolayer Ga might have contributed to the increased barrier height by 0.8 eV. We speculate that the increased coverage (>1 ML) of Ga quenches some of the surface states, thus shifting the neutrality level toward E_f so as to approach Schottky–Mott value of $\varphi_b \approx 0.6$ eV. The formation of a barrier at 1 ML suggests that the substrate surface has semiconducting character. This abruptness can be attributed to two plausible reasons, which may be mutually competing, (i) smallness of cluster size and incomplete band structure of Ga or (ii) a metallic to semiconducting phase transition of the substrate Si. We have deconvoluted Ga core levels to explore the possibility of the role of cluster size (FWHM) and incomplete band structure, and LEED to observe any surface structural phase transition.

Figure 2(b) shows the variation of the full width half at maxima (FWHM) of the Ga($3d$) core levels. The change in the branching ratio of Ga $2p_{1/2}$ and $2p_{3/2}$ has been presented as an inset of the Fig. 2, as a function of Ga coverage. The FWHM measured to be $\approx$1.6 eV for the initial Ga coverage, which suddenly assumes a value of $\approx$2.3 eV at the critical coverage of 1 ML. This change in the FWHM of 0.7 eV as shown in Fig. 2(b) can be attributed to an increased width of the transition level depending on the nature of the interface. Similar coverage dependence of the peak width has been reported earlier in literature,[15] and has been attributed to the formation of isolated metallic clusters at lower coverages, which after a critical thickness (due to the low mobility of adatoms at low temperature adsorption), forms the features typical of metallic Ga due to s-d hybridization. In the submonolayer regime, therefore the absence of any peak widening, could also be due to the pre-metallic dimensions of the Ga clusters. The sudden change in the Ga($3d$) peak width at 1.0 ML suggest a possible abrupt coalescence of 2D-clusters to form a metallic overlayer. The abruptness of the changes in the peak position and widths again discount the formation of an interface compound. The inset of Fig. 2 shows an interesting coverage dependence of the anisotropy of the intensities of the Ga core level spin-orbit split peaks of $2p_{3/2}$ and $2p_{1/2}$ transitions. The ratio of the intensities which is about 0.77 at coverage of 0.1 ML monotonically decreases with increasing Ga coverage and attains a saturation value of 0.66 at the critical coverage of 1 ML and remains unchanged for higher coverages. It has been argued in the past, that such anisotropic changes observed in Synchrotron XPS (SXPS) are due to the rapid variations in the cross sections around Cooper minima, which change the radial matrix elements and phase shift substantially, even for a small difference in the final state energies of $3d_{5/2}$ and $3d_{3/2}$.[16] In our experiments we have used conventional Mg K_α radiation with $h\nu = 1253.6$ eV in which energy regime such small KE changes have minimal cross section differences, so that such a process can be discounted. X-ray photoelectron diffraction studies have demonstrated this anisotropy as a manifestation of the inherent difference in the photoelectron wave functions of the two spin-orbit components ruling out significant inter-

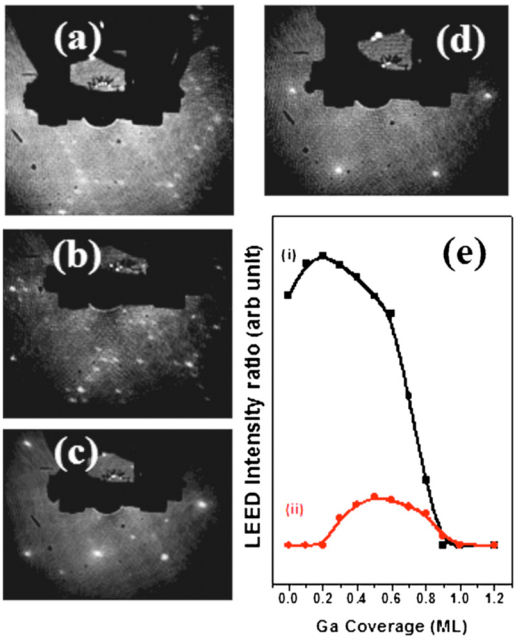

FIG. 3. (Color online) LEED pattern (63 eV) obtained for different Ga coverages adsorbed at RT onto Si(111)-7×7 surface. (a) Clean Si(111)-7×7, (b) $7\times7+\sqrt{3}\times\sqrt{3}$R30° at 0.4 ML, (c) $1\times1+\sqrt{3}\times\sqrt{3}$R30° at 0.9 ML, (d) 1×1 at 1.0 ML, and (e) plots Intensity ratio of the $1/7^{th}$ fractional order spot to integral spot (i) and $\sqrt{3}$ spot to integral order spot (ii) obtained for the various Ga coverages.

ference effects.[17] As the Ga adsorption proceeds in the submonolayer regime, the underlying (7×7) structure of the substrate remains intact up to 1 ML. The monotonic decrease in the anisotropy of the spin-orbit split peaks may be related with the increasing size of the premetallic 2D clusters.

The structural changes have been observed by LEED as shown in Fig. 3 during the room temperature adsorption experiments. Figure 3 shows some typical LEED pattern obtained at 0.0, 0.4, 0.9, and 1.2 ML Ga coverage, corresponding to 7×7, $7\times7+\sqrt{3}\times\sqrt{3}$, $1\times1+\sqrt{3}\times\sqrt{3}$, and 1×1 superstructural phases. The 0 ML coverage LEED shows a sharp hexagon of integral order spots and also the six fractional order spots between the integral spots, (manifesting the (7×7) reconstruction of the surface prior to Ga adsorption. To understand the changes induced in the surface phases, we have plotted the coverage dependence of the intensity ratio of the $1/7^{th}$ fractional order to integral spot and $\sqrt{3}$ to integral spot and as shown in Fig. 3(e). It is clear from the graph that the ratio increases up to the coverage of about 0.2 ML Ga coverage and for coverages greater than 0.7 ML the intensity ratio reduces sharply. At coverage of about 1.0 ML, the intensity ratio has decreased to a very low value, where only a (1×1) LEED is observed. The increase in the intensity of integral order spots has been observed, while the intensity of the $\sqrt{3}$ order spots increases from 0.3 to 0.5 ML and after that remains constant upto Ga coverage of 0.8 ML after which it falls to zero. This demonstrates that the adsorption of Ga does not disturb the underlying (7×7) substrate for submonolayer Ga coverages, but at coverage of 1.0 ML the (7×7) changes completely to the (1×1) surface phase.[13] The $\sqrt{3}$ phase is weak, and in localized regions. Since we observe the (7×7) to (1×1) change at 1 ML, the observation of an almost flat-band up to 1 ML in Fig. 2, can be attributed to the persistence of the metallic nature of the (7×7) structure of the substrate in the submonolayer coverage regime, which prevent the Schottky barrier formation. Thus, the persistence of the metallic (7×7) substrate reconstruction as 2D adatom clusters keep growing up to 1 ML, and consequently hinders the band-bending. Thus, we attribute another reason for this abrupt change to be a metallic to semiconducting surface phase transition of the substrate at 1 ML. The (1×1) semiconducting surface phase and the corresponding interface states create a barrier of 0.8 eV.

In summary our *in situ* experiments by surface sensitive electron spectroscopic and diffraction probes shows that the metallic Si(111)-7×7 structures remains intact and resists Schottky barrier formation upto 1 ML Ga Adsorption. For higher coverages, we observed a sharp transition in LEED, core-level peak positions, FWHM, and branching ratios. The resistance to band bending is seen to arise from the nonmetallicity of the submonolayer 2D Ga islands, which agglomerate into a flat layer at 1 ML coverage. LEED observations also show that the substrate symmetry sharply transits from the metallic (7×7) phase to the semiconducting (1×1) phase at the critical Ga coverage of 1 ML. Thus we attribute the changes to both the overlayer and substrate causes. For coverages >1 ML, the barrier height tends to attains the Schottky–Mott value, while the Ga(3*d*) FWHM and its branching ratio attain the respective bulk values. Further studies to quantify the contribution from both the sources are being probed by scanning tunnelling microscopy and spectroscopy studies.

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[1] E. F. Schubert, *Delta-doping of Semiconductors* (Cambridge University Press, Cambridge, 1996).
[2] K. Takayanagi, Y. Tanishiro, M. Takahashi, and S. Takahashi, Surf. Sci. **164**, 367 (1985).
[3] V. G. Lifshits, A. A. Saranin, and A. V. Zotov, *Surface Phases on Silicon* (Wiley, New York, 1994).
[4] H. H. Chang, M. Y. Lai, J. H. Wei, C. M. Wei, and Y. L. Wang, Phys. Rev. Lett. **92**, 066103 (2004).
[5] J. L. Freeouf, M. Aono, F. J. Himpsel, and D. E. Eastman, J. Vac. Sci. Technol. **19**, 681 (1981).
[6] J. Čechal, M. Kolibal, P. Kostelnik, and T. Sikola, J. Phys.: Condens. Matter **19**, 016011 (2007).
[7] M. Otsuka and T. Ichikawa, Jpn. J. Appl. Phys., Part 1 **24**, 1103 (1985).
[8] P. Kumar, M. Kumar, B. R. Mehta, and S. M. Shivaprasad, Appl. Surf. Sci. **256**, 480 (2009).
[9] K. Jithesh, Govind, U. V. Waghmare, and S. M. Shivaprasad, Appl. Surf. Sci. **256**, 348 (2009).
[10] M. Kumar, V. Govind, K. Paliwal, A. G. Vedeshwar, and S. M. Shivaprasad, Surf. Sci. **600**, 2745 (2006).
[11] Y. Enta, S. Suzuki, S. Kono, and T. Sakamoto, Phys. Rev. B **39**, 5524 (1989).
[12] M. Stampanoni, A. Vaterlans, M. Aeshlimann, F. Meier, and D. Pescia, J. Appl. Phys. **64**, 5321 (1988).
[13] V. K. Paliwal, A. G. Vedeshwar, and S. M. Shivaprasad, Solid State Commun. **127**, 7 (2003).
[14] K. D. Patel and R. Srivastava, J. Mater. Sci. Lett. **16**, 1509 (1997).
[15] K. Stiles and A. Khan, Phys. Lett. **60**, 440 (1988).
[16] M. Sieger, T. Miller, and T. C. Chaing, Phys. Rev. Lett. **75**, 2043 (1995).
[17] H. W. Yeom, T. Abukawa, Y. Takkakuwa, S. Fujimori, T. Okane, Y. Ogura, T. Miura, S. Sato, A. Kakizaki, and S. Kono, Surf. Sci. Lett. **395**, L236 (1998).