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Electronic structure of Yb/H–Si (111) interface*

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Photoemission spectra are measured for Yb covered surface of wet-chemically-etched H–Si (111). The results reveal that the lattice structure of the H–Si (111) surface is stable against the deposition of Yb atoms. X-ray photoemission spectra indicate the formation of a polarized (dipole) surface layer, with the silicon negatively charged. Ultraviolet photoemission spectra exhibit the semiconducting property of the interface below one monolayer coverage. Work function variation during the formation of the Yb/H–Si (111) interface is measured by the secondary-electron cutoff in the ultraviolet photoemission spectral line. The largest decrease of work function is ∼1.65eV. The contributions of the dipole surface layer and the band bending to the work function change are determined to be ∼1.15eV and ∼0.5eV, respectively. The work function of metal Yb is determined to be ∼2.80±0.05eV.

Keywords: Yb/H–Si (111), photoemission spectra, electronic structure, work function
PACC: 7320A, 7330, 7340N, 6848

1. Introduction

Like most surfaces of covalent semiconductors, Si (111) reconstructs itself in order to lower the high surface energy associated with dangling bonds.[1−4] In order to examine the electronic bulk structure of silicon through its (111) surface and for some technical reasons, it is necessary to avoid surface reconstructions. HF acid etched Si (111), H–Si (111), has been proven to have an ideal unreconstructed surfaces.[5,6] Electronic structure of H–Si (111) surface was well-established by photoemission spectra (PES) measurements[6−8] and used as an testimony of theoretical calculations. H–Si (111) surface is also of importance in the semiconductor industry as HF treatment is usually performed prior to the growth of gate oxide. It can also be used as a valuable substrate surface to grow epitaxially well-oriented layered compounds.[9]

To exploit the applications of H–Si (111), it is essential to investigate the electronic structures of the surface upon the deposition of other atoms or molecules. This is a new realm in semiconductor physics and condensed matter physics. Few pioneer works have been reported.[10−13] The results revealed that the Si–H bond could break or remain stable, depending on the adsorbed atoms or molecules, which resulted in various surface electronic structures and epitaxially growing mechanisms. In this article, we extend the research works to rare-earth (RE) metal deposited H–Si (111) surface by core-level, valence band and work function measurements using photoemission technique. We select ytterbium as the first among the RE/H–Si (111) systems because Yb silicides formed at naked Si surfaces have been investigated in some detail.[14−17] The results can help us in the analysis of the PES results in this work. Besides, Yb is, to the best of our knowledge, one of the very few elements in the periodic table whose work function has not been measured yet. We will acquire the work function on a thick Yb film by measuring the secondary-electron cutoff of the ultraviolet photoemission spectral line.

2. Experiment

The Si (111) wafers (p-type doped) were offered by the State Key Laboratory of Silicon Materials of Zhejiang University. After being ultrasonically cleaned in deionized water and ethyl alcohol, the wafer was rinsed sequentially in solution 1 ($NH_3{\cdot}H_2O$:H_2O_2:H_2O=1:1:6, 80 °C, 15min) and solution 2 (HCl:H_2O_2:H_2O=1:1:6, 80 °C, 15min). After being washed in deionized water, the wafer was

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etched in 5% HF for 1min. Then, the wafer was rinsed in deionized water for less than 5 s to remove residual compounds from the etching process. The resulting H–Si (111) was clamped onto a Mo sample holder and put into the ultra-high-vacuum system in less than 5min. We prepared two H–Si (111) samples by the above procedure for x-ray photoemission spectrum (XPS) and ultraviolet photoemission spectrum (UPS) measurements, respectively.

Yb depositions and PES measurements were performed in a multifunctional ultra-high-vacuum system (Omicron Instruments for Surface Science) with a base pressure better than 2×10^{-8} Pa. The system consists of a fast entry, a preparation chamber, and two analysis chambers. In the present work, UPS measurements were performed with the UV lamp of He I (21.2eV) and a sample bias of –5.0V. XPS measurements were carried out with an Mg Kα source (1253.6eV). An integrating hemispherical electron-energy analyser was used to collect the photoelectrons. The emission angles of the photoelectrons were $\sim55^\circ$ and $\sim42^\circ$ for UPS and XPS measurements, respectively. The overall energy resolution was $\sim$0.1eV for UPS, while the energy resolutions for XPS measurements depend on the pass energy adopted to acquire sufficient spectral intensities.

Yb was evaporated from a Ta boat located $\sim$11cm away from the sample surface. The high-purity Yb (99.99%) was purchased from Beijing Research Institute for Nonferrous Metals. Yb source and the HF acid etched Si wafers were thoroughly degassed. The clean and well-ordered surfaces of the H–Si (111) wafers were checked by low energy electron diffraction (LEED) and XPS measurements. The LEED pattern exhibited the clear and bright (1×1) diffraction spots for the H–Si (111) surface. The O 1s signal was negligible, and the C 1s signal was entirely undetectable in the XPS measurement. It should be mentioned that the procedure of preparing the H–Si (111) surface described above is different from that of preparing the atomically smoothed H–Si (111) surface.[5,6] There should be some atomic-level roughness on the surface although we observed the (1×1) LEED spots. However, these defects do not affect the conclusions of this article.

3. Results and discussion

3.1. Core-level x-ray photoemission spectra

The XPS measurements were carried out to investigate the core-levels of Si and Yb. Curves *a* and *b* in Fig.1 show the results of the original and the 6nm-Yb-covered H–Si (111) surfaces, respectively. Sixty angstrom is the greatest coverage of Yb in the XPS studies in this work. Curve *c* and the inset were measured for another sample, and will be discussed in Section 3.3. The thickness of Yb film was estimated based on the attenuation of Si 2s signal (Si 2p gave almost the same results) and the inelastic-mean-free-path ($\lambda_{\rm in}$) of the electrons through the Yb film.[18,19] Due to the scarcity of experimental value of $\lambda_{\rm in}$ for Yb, we performed a calculation with the method proposed by Tanuma *et al.*[19] The calculated value was $\sim$3.9nm.

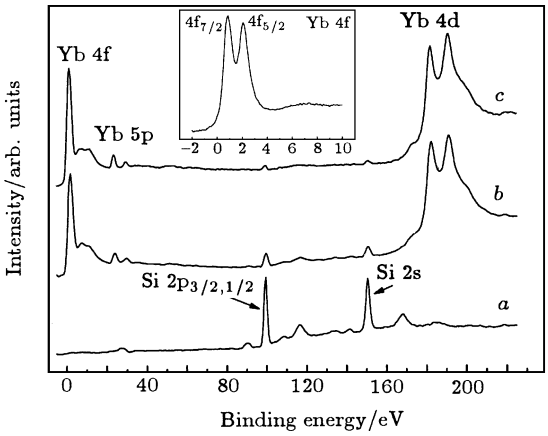


Fig.1. XPS of clean (curve *a*), 6nm-Yb-covered (curve *b*) and 10.5nm-Yb-covered (curve *c*) H–Si (111). Curve *c* was measured to determine the work function of metal Yb in Section 3.3. Pass energy of the electron-energy analyser is 50eV for all the three lines. The inset shows the separate spin-orbital splitting of $4f_{7/2}$ and $4f_{5/2}$ recorded for the 10.5nm-Yb-covered sample with the pass energy of 10eV.

Deposition of Yb on naked Si surface usually results in the formation of various phases of silicides.[16] As for the H-terminated-Si surface, the case might be different. Some reported results[20,21] have shown that the Si–H bond can either prevent the bonding of Si with the adsorbed metal atoms or break upon the adsorption of some other metal atoms.

Figure 2 exhibits the successive evolutions of Si 2p (left panel) and Si 2s (right panel) upon the deposition of Yb atoms. The spectral lines are recorded with the pass energy of 50eV. The large pass energy enables us to acquire sufficient spectral intensities even with tens of angstrom of Yb covering the sample surface, although the energy resolution is relatively low. The spin-orbital splitting of Si $2p_{3/2}$ and $2p_{1/2}$ is not resolved in the figures. In Fig.2, Si 2p and 2s core-levels

move to higher binding energy by the same amount of ~0.5eV with ~0.3nm Yb (0.32nm corresponds to one monolayer (1ML) coverage on Si (111) surface[16]) on the sample surface. More depositions make the intensities of Si 2p and 2s decrease continuously. The movements remain unvaried with ~0.5nm coverage. When the coverage is larger than ~1.3nm, Si 2p and 2s move backwards slightly due to the screening effect by the metallic Yb overlayers. These observations differ from the case for silicides where Si 2p moved to lower binding energies by more than 1eV.[16] Thus the movement of Si 2p and 2s implies that the H–Si (111) surface is stable against Yb adsorption. Another more direct evidence of the stable H–Si (111) surface is that we could observe the Si–H bonding states in the UPS measurements after large amount of Yb covering the sample surface (see Section 3.2). Additionally, the (1×1) LEED spots could still be observed at ~1.3nm coverage without the formation of any additional reflections, although the spots were blurred (the incident electron energy is 35eV). On the other hand, only ~0.1nm adsorption of Yb on Si (7×7), where the silicides formed, could damage the (7×7) LEED spots.[16] The LEED result thus exhibits the unchanged lattice structure of the H–Si (111) surface, which coincides with the XPS and UPS results. Thus we can safely conclude that the H–Si(111) surface is stable against Yb adsorption.

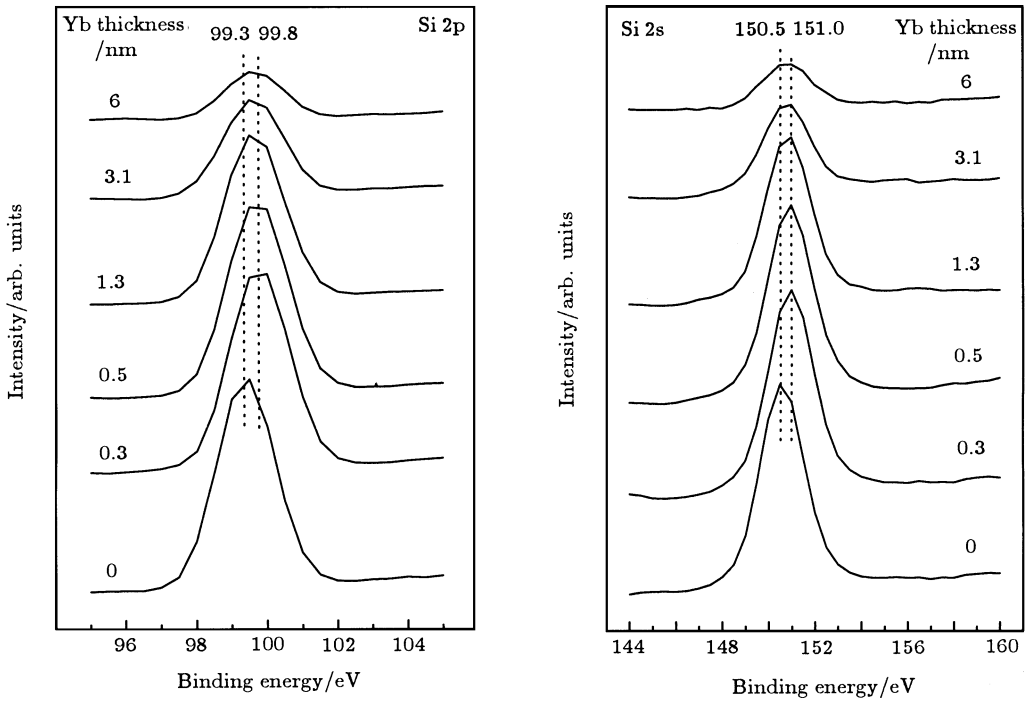


Fig.2. Si 2p (left panel) and Si 2s (right panel) core-level evolutions upon Yb depositions. The film thickness labelled next to the lines was determined by the attenuation of the Si 2s signal.

The core-level movements in Fig.2 can only be interpreted as by band bending. It is well known that the contact of metal with p-type semiconductor makes the energy band near the interface bend downwards, which results in the core-level movement to higher binding energy. The movement is a measure of the band bending.[22,23] Accompanying the band bending, the adsorbed metal atoms can also create a polarized surface layer. With reference to the discussion[22] about the case of Cs adsorption on H–Si (111) where Si 2p moved to higher binding energy by ~0.4eV, we reach the conclusion that Yb adsorbed on H–Si (111) creates a strongly polarized interface layer with Si negatively charged. The polarized layer should affect the work function of the interface. In Section 3.3, we will offer the work function evidence, besides the core-level movements, for existence of the polarized interface layer.

3.2. Valence band ultraviolet photoemission spectra

We measured the UPS of the Yb-covered H–Si (111) from 0 to ~10.5nm coverage. The left panel of Fig.3 shows the UPS lines in the energy range from the Fermi level (E_f) to 15eV below E_f. The right panel

enlarges the spectral lines in the vicinity of E_f. The thickness for the thickest Yb film was determined by the intensities of Si 2p and Yb 4d XPS peaks measured after the UPS measurements. The XPS result is shown in Fig.1 (curve *c*). Curve *c* was also recorded with the same pass energy of 50eV as that of curves *a* and *b* to make the lines comparable. The inset in Fig.1 gives the spin-orbital splitting of $4f_{7/2}$ and $4f_{5/2}$ measured with the pass energy of 10eV corresponding an energy resolution of ~0.9eV (full width at half maximum for C 1s[24,25]). We normalized curve *b* and *c* to the height of the Yb 4d peak in Fig.1. The Si 2p and 2s signals in curve *c* are very weak as compared to curve *b*. The latter corresponds to a thickness of ~6nm (see Section 3.1). A quantitative analysis of the Si 2p intensities in the two curves indicated a thickness of ~10.5nm for the thickest Yb film in the UPS studies. Yb film thickness for intermediate coverages is, however, difficult to estimate because we adopted different electric currents through the Ta boat for each trial. Only the coverage near ~1 ML (curve *f* in Fig.3, see Section 3.3) can be estimated by the work function measurements. The reason why we adopted different electric currents is that one of the main purposes of this work is studying the electronic structure evolutions of the Yb/H–Si (111) interface. The evolutions should be investigated starting from the coverages below 1 ML. We started from a very low current of 5.8 A through the Ta boat to acquire the coverages below 1 ML (no Yb could be detected by XPS and UPS with electric currents less than 5.8 A for the Ta boat used in this work). However, using the low electric current, it is rather time-consuming to prepare thick film. Thus we gradually increase the current up to 7.8 A to prepare a thick Yb film for the work function determination of metal Yb.

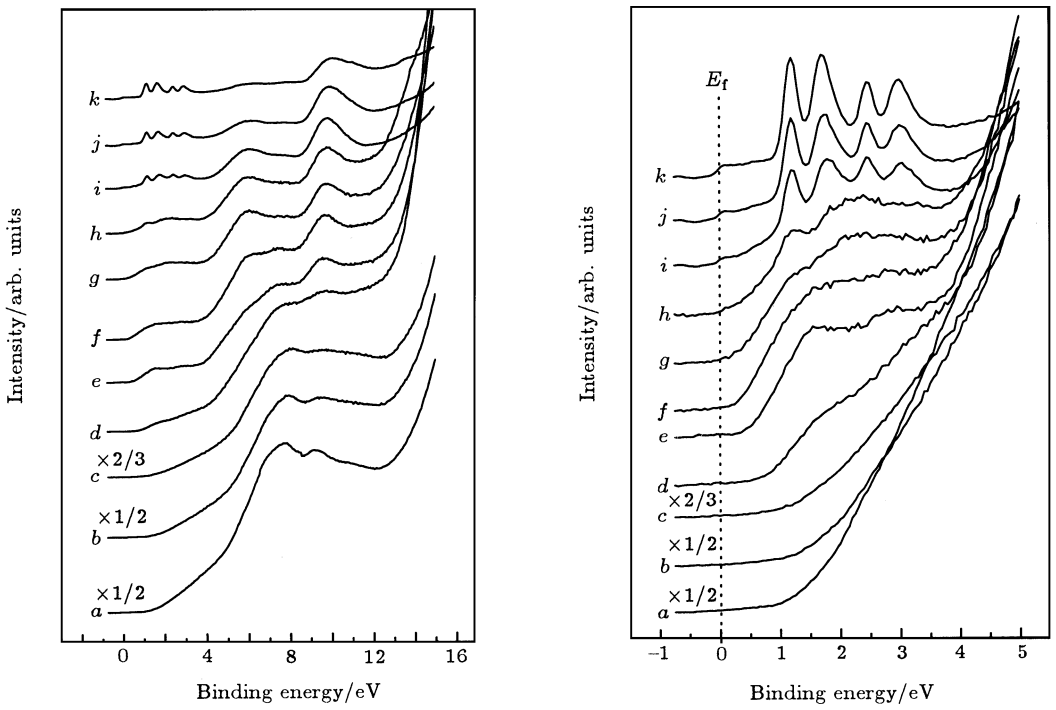


Fig.3. Valence band evolution of Yb-covered H–Si (111). The electric currents through the Ta boat and the time for each deposition trail are as follows: *b*-(5.8 A, 10min); *c*-(5.8 A, 20min); *d*-(6.1 A, 20min); *e* and *f*-(6.4 A, 20min); *g* and *h*-(6.6 A, 20min); *i*-(6.8 A, 20min); *j*-(7.3 A, 20min); *k*-(7.8 A, 30min). Curve *a* represents the UPS line of clean H–Si (111). Curve *f* corresponds to the coverage of ~1ML (0.32nm) determined by the work function measurements, and the coverage for curve *k* is determined to be ~10.5nm by the XPS measurements.

Before discussion of the valence evolutions as shown in Fig.3, we wish to first analyse the UPS for the clean H–Si (111) surface. The valence band structure has been thoroughly studied by the angle-resolved UPS (ARUPS) measurements[6−8,26,27] on well-ordered H–Si (111) samples. The reported ARUPS results can help us to understand the results of the angle-integrated UPS (AIUPS) in Fig.3. The spectral weight between ~1.0eV and 5.0eV are derived from two bulk states. The spectral weight between 6.5eV and 8.0eV are derived from two other bulk states. There are two surface states between 5.0

and 6.0eV. One of them with the lower binding energy corresponds to the bonding between surface Si and bulk Si. The other corresponds to the surface Si–H bonding (Si 3p–H 1s bonding) state. The spectral feature located at ~9.3eV is the surface hybridizing state between H 1s and Si 3s.[25] A weak feature located at ~11eV was also observed by the ARUPS measurement,[7] but has not been interpreted yet.

In Fig.3, the photoemission from H–Si (111) decreases its intensity with increasing amount of Yb on the sample surface. The features near 6.0 and 10.0eV, which correspond to the surface states, persist even with ~ 10.5nm Yb deposited. This observation reveals undoubtedly that the Si–H bonding is stable against Yb adsorption, as mentioned in Section 3.1. The bulk Si–Si bonding states decrease their intensities more rapidly than the surface ones due to the fact that their photoelectrons must pass through larger distance in the sample as compared to the surface state photoelectrons.

As for the electronic states in the vicinity of the Fermi level, there is no electron occupation at E_f below ~1ML Yb coverage (curve f). Thus, the Yb/H–Si (111) interface has the semiconducting property, which is different from the metallic Yb/Si (7×7) interface and silicides.[16] The spectral weight at E_f can be observed from curve g, which indicates that the Yb atoms start to metallize above 1 ML coverage. For thick Yb film (curve k), the two peaks located at 1.2 and 2.5eV correspond to the spin-orbital doublets of $4f_{7/2}$ and $4f_{5/2}$ of bulk Yb atoms. The two peaks located at 1.7 and 3.0eV are the spin-orbital doublets of the surface Yb atoms[28,29] (these two surface states cannot be observed in the XPS measurements (the inset of Fig.1) due to the different information depth for UPS and XPS[30]). Compared to the thick Yb film, thin Yb film (curves f through h) shows near flat line shapes for Yb 4f state. Below 1 ML coverage (curve b through e), Yb 4f states have higher binding energies as compared to the thick film. These observations exhibit that the Yb 4f states are sensitive to chemical environment although they belong to inner shells. Indeed, drastically different 4f PES structures were found for Yb in different compounds (including silicides).[16,31–33]

3.3. Yb-induced work function change

Work function Φ is an important parameter for the metal–semiconductor interface. In this work, we measure the work function by the secondary-electron cutoffs of the UPS lines. The uncertainties of the measured values are estimated to be ~0.05eV according to the energy resolution of the spectrometer and the sharp cutoffs.

Figure 4 exhibits the cutoffs for the Yb adsorbed H–Si (111). Spectral lines in Fig.4 and the corresponding lines in Fig.3 were recorded simultaneously. The parts with binding energies higher than 14.0eV were cut out for the work function studies. The work function values next to the lines were determined from the cutoff tails. The clean H–Si (111) has a Φ of 4.15eV. Φ decreases rapidly to its minimum (2.50eV) with minor amount depositions of Yb, as in the cases of metal atom adsorbed p-type semiconductor. With more Yb deposited, Φ increases gradually. The work function for ~10.5nm Yb has a value of 2.80eV. This value is the first experimental value of work function for metal Yb, which supports the theoretical work of Durakiewicz *et al.*[34]

Work function measurements are widely used as a method to calibrate the coverage of adsorbed atoms (molecules) on condition that the adsorbed atoms (molecules) do not combine with the substrate. Strictly, this method can only calibrate the coverage of ~1 ML without the assistance of other techniques or knowledge (the case of this work). One monolayer in this calibration method is defined as the coverage corresponding to the Φ minimum.[35] This definition coincides fairly well with other methods.[36–39] The minimum of Φ corresponds to curve f in Fig.4. Thus, curve f in Figs.3 and 4 corresponds to the coverage of ~1ML, as mentioned several times in Section 3.2.

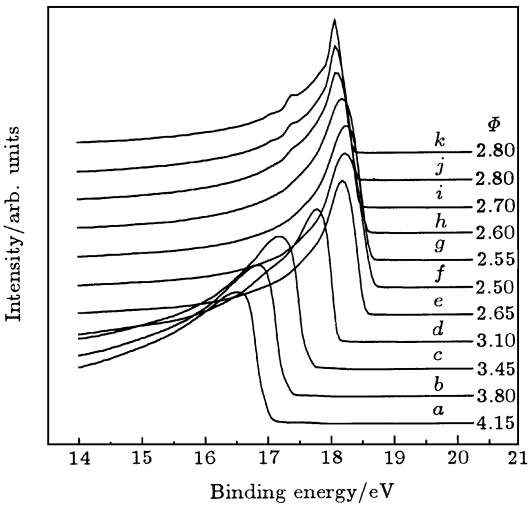


Fig.4. Normalized secondary-electron cutoffs and work functions of the Yb adsorbed H–Si (111).

For metal–semiconductor interface, the work

function change, $\Delta\Phi$, can be expressed as

$$\Delta\Phi = \Delta V_{\rm sd} + \Delta V_{\rm bb},$$

where $\Delta V_{\rm sd}$ denotes the change of the surface dipole layer, and $\Delta V_{\rm bb}$ denotes the band bending.[39] The greatest decrease in Fig.5 is 1.65 (= 4.15 – 2.50)eV. The XPS results (Section 3.1) have determined the band bending to be ∼0.5eV. The magnitude of the band bending is not enough to explain the decrease in work function. Thus, the work function change, besides the core-level movements discussed in Section 3.1, reveals the existence of the polarized interface layer. The contribution of the surface dipole layer to the work function change can be deduced to be ∼1.15 (=1.65 – 0.5)eV.

The increase of Φ after the minimum is due to the metallization of Yb atoms that results in the depolarization effects. In Fig.3, the metallization starts at curve *g*, i.e. there is spectral weight at the Fermi level, in good agreement with the Φ minimum shown in Fig.4.

4. Conclusion

In summary, H–Si (111) is stable against the adsorption of Yb and maintains the semiconducting property below 1 ML coverage. The significant effects of Yb on H–Si (111) are as follows. First, a dipole interface layer forms with Si negatively charged. Second, the work function decreases from 4.15eV to 2.50eV with 1 ML coverage. The contribution of the dipole layer and the band bending to the work function decrease are ∼1.15eV and ∼0.5eV. The work function of metal Yb is ∼2.80eV.

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