Adsorption and Reaction of Calcium at the Si(111) Surface Studied by Metastable-Induced Electron Spectroscopy

Yasuo Shirouzu, Yoshinori Kaya, Tomokazu Okazaki, Akihiko Watanabe, Masamichi Naitoh, and Satoshi Nishigaki
Department of Electrical Engineering/Electronics, Kyushu Institute of Technology, Sensui 1-1, Tobata, Kitakyushu 804-8550, Japan

Tomonori Ikari
Ube National College of Technology, Tokiwadai 2-14-1, Ube, 755-8555, Japan

Kenji Yamada
Ishikawa National College of Technology, Tsubata, Ishikawa 929-0392, Japan

(Received 6 December 2006; Accepted 15 March 2007; Published 27 March 2007)

I. INTRODUCTION

Although many III-V semiconductors are used by preference in optoelectronic devices, they would be replaced by some other types of semiconductors in the near future owing to their inherent drawbacks [1]. Mostly they are composed of scarce elements utilizable on the earth. Those sometimes form materials being dangerous to the human bodies. Most III-V semiconductor crystals are difficult to be epitaxially grown on the Si surfaces. Nitrides of group-III elements and some metal silicides are candidates for such optoelectronic materials as being compatible with the earthly environments. Calcium silicide is one of those promising materials. There are several stable phases in this kind of silicides, among which only the Ca$_2$Si phase is semiconductive with a direct band-gap in the visible-light regime ($\lambda = 653$ nm). The solid-phase reaction in Ca-Si interfaces has scarcely been studied so far [2-5]. However, it is to be desired that such reactions should be investigated in order to find conditions to ensure its epitaxy on Si surfaces.

The valence electronic state of an atom in a solid is expressed by a certain valence-state configuration. For Si, the sp$^2$ configuration is possible, by separating one p-state, which leads easily to a planar bonding like the honeycomb structure. If the s-state is isolated, the remaining ones should nearly be of pure-p states. Then, at the surface, Si backbondings may be formed with angles of $\pi/2$ between them [6]. These bondings must be important elements in the reconstruction of Ca-adsorbed Si surfaces [7–11]. Moreover, some drastic effect of these electronic configurations may be possible on the Ca-Si compound formation [12]. When a Si3s-state becomes isolated from the band, the number of remaining valence electrons is two. The Si disguises itself as a divalent atom, and, in a sense of divalency, Si resembles calcium. Then, the Ca-Si compound becomes nearly equivalent to a solid Ca that would be compressed because it contains atoms with smaller radii (Si). It may undergo metal-semiconductor transition similar to a reported metal-semimetal transition in Ca under high pressure [13]. This expectation is found to have reality according to reported electronic-structure calculations [12, 14, 15], which demonstrate that Ca$_2$Si is quite distinctive from the others: The Si3s-state becomes isolated from other bands at the binding energy of about 7 eV. Concerning this isolated s-state itself, the binding-energy value 7 eV is a keyword in analyzing the spectra, because the energy of the isolated atomic states is, in principle, not changed by the surroundings.

We have studied adsorption of Ca on the Si(111) surface and their interface reactions by metastable-induced electron spectroscopy (MIES). This spectroscopy shows extremely high sensitivity to surface-localized electronic states. In this paper we will present evidence for a solid-phase reaction in the Ca/Si interface to produce partially Ca$_2$Si-like phases in a temperature range around 570 K. Moreover information concerning surface-localized states being characteristic of Ca-induced reconstructions of the Si(111) surface are obtained and discussed with reported

---

*This paper was presented at The 7th Russia-Japan Seminar on Semiconductor Surfaces (RJSSS-7), Vladivostok, Russia, 18-20 September, 2006.
†Corresponding author: e346423y@tobata.isc.kyutech.ac.jp
structure models.

II. EXPERIMENTAL

A. Apparatus

The sample is a Si(111) substrate of B-doped p-type with resistivity $\sim 2 \Omega \text{cm}$, cleaned in a vacuum by direct-current Joule heating, yielding clear $(7 \times 7)$ LEED patterns. Calcium was evaporated with a heated tantalum crucible, and deposited on the Si(111) surface at rates of the order 1.5 ML/min, where ML is the surface atomic density of Si(111). After the Ca deposition the sample was annealed in steps of 10 minutes at increasing temperatures.

Helium atoms were excited by hot-cathode low-voltage discharge to the metastable states (He$^*$), of which about 90% was in the 2S state [16]. Particles like fast atoms or photons, produced by the discharge, were discriminated from metastable atoms by their time-of-flight differences. Kinetic energies of electrons emitted from the samples (biased by $-15.0$ V) are measured by a retarding-field energy analyzer. The row data of its output, forming integrated spectra, were numerically differentiated to yield MIES spectra.

B. Auger processes in MIES

Many channels are open to the de-excitation of metastable atoms at surfaces [17], among which two processes are relevant to the present experiment: At a high work-function surface, as the clean Si, metastable atoms undergo resonance ionization followed by Auger neutralization (RI+AN); On the other hand, at surfaces that show low work function or appropriate energy-gaps, the Auger de-excitation (AD) occurs, and only one hole is created in the surface band in spite of the Auger transition. In the latter case, the electron spectra reflect directly the local density of states at positions where He$^*$ atoms are de-excited.

III. RESULTS AND DISCUSSION

A. Reaction at a deposited Ca(1 ML)/Si (111) interface

At first, we applied the MIES method to a reacting Ca+Si system at temperatures above RT and obtained a series of spectra shown in Fig. 1. The bottom spectrum (a) was obtained from the clean Si(111) surface, and the second one (b) from a Ca as-deposited surface at a coverage of about 1 ML. The low-energy threshold of the spectrum, which corresponds to the surface local-potential barrier, was shifted markedly to lower energies in spectrum (b). The work function was, therefore, decreased by the adsorption of Ca on the Si surface. This means that alkaline-earth metals also show a character of electron donation to their bonding partners like alkali metals do. The spectra (b)-(f) showed abnormal fluctuations in intensity below the threshold energy in spite of the expectation of zero intensity. The spectral shape in that energy region was not reproducible. We are not sure about its origin, but suppose that it may reflect some inhomogeneity in the composition of the annealed surface, or may be due to a complexity in the surface local potential especially of Ca-Si compound surfaces. The global threshold behavior of the spectra reflects the potential barrier which passes electrons from the subsurface region to the vacuum. However, there are excitations of electrons, in the MIES, at places just in front of the topmost atomic layer where the local potential may differs from its average. Since we have no further facts to endorse such an argument, we defer the decision of this question to future studies. This should not influence much the whole discussion on the spectral structures at energies above the threshold.

The high-energy cutoff in the spectrum from the Cadsorbed surface appeared at a higher energy than the spectrum from the clean surface. This means that the mechanism of electron emission is converted into the AD process at Ca-adsorbed surfaces. Therefore, for Cadsorbed surfaces, this high-energy cutoff is regarded as the $E_F$ from which the binding energy is measured. Spectrum (b) contains many structures, contrary to a naive ex-
pectation of some simple-peak structure near the Fermi level as the case of alkali-metals [18], based on the same idea of weak interaction. This result means that, even at RT, adsorbed Ca interacts with the Si substrate.

When the surface was annealed at temperatures 470-770 K, we got spectra (c)-(f) which show 4 peaks, P1-P4, together with a peak Ps at binding energy of about 7 eV. The intensity of Ps is not large, but is confirmed to be reproducible. The binding energies for peaks P1 and P2 were about 9.5 and 12 eV, respectively, but those for P1 and P2 were shifted from about 2 to 4 and from about 5 to 6 eV, respectively, by increasing the temperature. They are explained by referring published bulk electronic-structure calculations for various Ca-Si compounds [12, 14]. The calculated density-of-states (DOS) curves show a low binding-energy (BE) band that involves components of Si-p and Ca-sp, common to the three compounds: Ca2Si, CaSi and CaSi2. This band is widened upon increasing Si content and, therefore, its mean BE is shifted from about 1.5 to 3 eV in this order of compounds. Peak P1 corresponds well to this band. This peak was rather weak in intensity compared with other peaks. This may be explained by a matrix element effect for the AD process where transitions from initial states involving p- or d-states contribute weakly to the MIES spectrum. The calculations [12, 14] also show a higher BE band involving Si-sp states with two prominent DOS peaks at about 6 and 9 eV for CaSi, and a similar band whose bottom shifts down in energy reaching BE=12 eV in CaSi2. Observed peaks P2, P3 and P4 in Fig. 1 correspond to those theoretical bulk-DOS peaks. For identifying peak Ps which appeared only for surfaces annealed at lower temperatures, we again refer to the reported DOS calculation [12, 14]. It may correspond to the isolated Si 3s-states characteristic of the Ca2Si phase. Present attribution of the MIES peaks suggests that annealing at lower temperatures of about 470-570 K produces Ca2Si-like phase on the Ca/Si interface, and that, at higher temperatures, Si-rich phases are formed. A. Schöpke, et al. reported that the Ca-rich phase is formed at temperatures up to 598 K and the CaSi2 growth takes place above 673 K [4]. Our present results are consistent with their results.

The MIES spectrum was changed drastically when the surface was annealed at temperatures around 870 K as shown in Fig. 1(g). As described in the next subsection, the LEED experiment demonstrated a formation of ordered surface phases at such high temperatures. Therefore we conclude the layers have been decomposed to partially evaporate Ca out of the surface at temperatures higher than about 800 K.

**B. Variations in LEED**

In a LEED experiment, Ca-Si compounds in the condition of (c)-(e) in Fig. 1 did not give any diffraction structures relating to ordered phases. Therefore we judge that long-range-ordered phases of silicide are not formed by the present procedure of RT-deposition followed by annealing at moderate temperatures, although solid-phase reactions surely occur at these temperatures. Ordered LEED patterns were observed only when the annealing temperature increased roughly above 800K. The surface of (e) in Fig. 1 exhibited a 5×1 LEED pattern.

In order to investigate in detail surface-phase transition depending on the Ca coverage, we used a surface with a small deposit of Ca (0.6 ML) for avoiding Ca-Si compound formation. Fig. 2 displays corresponding LEED patterns showing 2×1, 5×1 and quasi-3×2 reconstructions. The 2×1 structure appeared at 770-820 K, the 5×1 at 830-840 K and the 3×2 above 850 K. These temperatures are lower than that for the case (e) of Fig.1. In the latter condition, Ca-Si compounds were formed and, therefore, higher temperatures were necessary for decomposing them before inducing reconstructed surface phases. Note here that the annealing time was adjusted for the same period interval (10 minutes) for both the samples. The present observation of surface phase transition is almost the same as the studies already reported in the literature [7–11]. According to proposed models for the atomic structure of Ca-induced surface phases [7–11], the structure that exists in the 5×1 and the quasi-3×2 structures but does not in the 2×1 phase should be the honeycomb chain channels. What they call Seiwatz chains are formed in the 2×1 and 5×1 phases. These reconstructions need their characteristic bonding schemes, which would express different spectral features correlating with the structure.
FIG. 3: A series of MIES spectra obtained from a Ca(0.6 ML)-covered Si(111) surface being annealed at temperatures 820-860 K.

C. MIES for three different Ca/Si(111) phases

We obtained MIES spectra, shown in Fig. 3, from three different phases in a sequence of decreasing Ca coverage. The spectra tell again that the metastable spectroscopy seems to be weak in an energy region near EF in comparison with the photoemission method [9, 19–21]. Photoemission data are usually analyzed in bringing the structures near the Fermi level into focus, from certain interests, for instance, to find metallic or semiconductive features at the Fermi level [9, 19–21]. Present MIES spectra obtained from the quasi-3×2 surface (curves (c)-(f)) also look to show some semiconductive feature: very weak emission intensity near EF.

Concerning structures at relatively high binding energies, the MIES spectra from 5×1 and quasi-3×2 resemble each other, but do not resemble the spectrum from the 2×1 phase. A peak, labeled P_s, appeared in either phase reproducibly at the binding energy of about 7 eV, although its intensity was varied considerably. Another peak, labeled P_p, appeared at about 9.5 eV clearly in the 5×1 and 3×2 phases. There may exist a shoulder in the 2×1 phase (spectrum b) although shifted in energy from P_p of the spectra (c-f). It is rather weak in intensity.

By referring reported structure models for the three surface phases [7–11], we assume the peak P_p at higher binding energies, which appeared strongly in the 5×1 and the 3×2 phases, corresponds to the bonding states of sp²-based planar orbitals. The construction of those phases needs the honeycomb structure, but the 2×1 phase does not. Since we can expect that a honeycomb-type bonding with these orbitals will be strong, our assignment of peak P_p with relatively high binding energies to those bonding states seems reasonable.

On the other hand, peak P_s would be attributed again to some isolated s-states owing to its binding energy value, about 7 eV. The separation of the s-state tends to lead the remainder to the p-states. It helps Si in forming back-bondings with angles of about π/2 between them. This element is necessary in the formation of so-called Seiwatz chains in both the 2×1 and the 5×1 phases. Such chains are not necessary in the 3×2 phase. However, in the unit of honeycomb structure, Si atoms at either of two sites out of six need backbondings with subsurface atoms in a similar geometry to the Seiwatz chain. This consideration is consistent to the observation in Fig. 3 that the peak P_s appeared in either phase.

There exist unidentified structures in the observed MIES spectra. Especially an origin for a peak marked in dotted line in the spectrum (b) of Fig. 3 is requested to be clarified. In order to confirm the attribution that we attained by the present experiment, one should do some electronic-structure calculation, and in fact we are preparing it.

IV. CONCLUSION

We confirmed that the Si substrate reacts with adsorbed Ca even at RT, and that annealing of this Ca/Si interface at 470-570 K causes chemical reaction which induces formation of surface compounds similar to Ca₂Si. For the formed surface compounds, MIES detected successfully a feature corresponding to the narrowed Si-3s band at BE≈7 eV characteristic of the formed surface compound. By annealing at higher temperatures, surface compounds are desorbed, and Ca-induced phases (2×1, 5×1, quasi-3×2) are produced. Each phase contributes MIES spectra by its characteristic electronic structures correlating with the local bonding geometry.

Acknowledgments

This work has been supported by Grants-In-Aid from the Ministry of Education, Science, Culture and Sports of Japan.


http://www.sssj.org/ejssnt (J-Stage: http://ejssnt.jstage.jst.go.jp)


