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Formation of two-dimensional uranium silicide film and its electronic structure study

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ABSTRACT

Uranium (U) deposition onto the Si (1 1 1) − 7 × 7 surface followed by annealing at 870 K for 6 min leads to the formation of 2D uranium silicide ($USi_{1.67}$) film. The morphology and geometric structure have been studied by scanning tunneling microscopy (STM), low-energy electron diffraction (LEED) and reflection high energy electron diffraction (RHEED). The AlB_2-type structure of $USi_{1.67}$ epitaxial film is formed with a 1 × 1 periodicity. Morphologies of the crystalline $USi_{1.67}$ film display triangular layered structures, and its electronic structure has been studied by a combination of angle-resolved photoemission spectroscopy (ARPES) and density functional theory calculations.

1. Introduction

Rare-earth silicides (RE=Y, Er, Gd, Dy, Lu, and Ho) epitaxially grown on Si (1 1 1) substrates have been the focus of considerable attention in recent years, due to their low Schottky barriers (0.3–0.4 eV), and small lattice mismatches with Si (usually far less than 1%) [1–7]. One important research field of the RE silicides is the formation of two-dimensional high quality films, which is an important factor in the quality control of microelectronic devices. Even though uranium silicides are not very likely to be included in the metal/semiconductor interface of the microelectronic device, a detailed understanding of their properties is nevertheless very important to gain some insight into the parameters which control these properties. Meanwhile, the discovery of the superconductor MgB_2 with the highest T_c among intermetallic compounds (T_c=39 K) [8] has stimulated the search for new superconductors in the AlB_2-type (space group P6/mmm, No.191, Z=1) compounds, such as the binary silicides $ThSi_2$ [9] and USi_2 [10,11]. However, uranium silicides, promising nuclear fuels, remain an unexplored field as yet in surface science both because of the radioactivity and difficulties in sample preparation. Only a few studies have been made on the U–Si system [12–16]. Fujimori first reported the study of uranium deposition onto the well-ordered Si (1 0 0) and Si (1 1 1) surfaces by X-ray photoelectron spectroscopy (XPS) [14,15], and proposed that if the U/Si (1 1 1) interface was annealed at 700 °C, clear LEED spots may be observed, suggesting the possible formation of ordered uranium silicide phases at the interface [14].

The purpose of the present study is to search for possible epitaxial growth of uranium silicide phases on the silicon surface, and perform angle-resolved photoemission spectroscopy (ARPES) experiments on them, which will give a better understanding of the character of U 5f electrons in these systems. In this work, 2D $USi_{1.67}$ film was first successfully obtained by deposition of 3 ML U on Si (1 1 1) − 7 × 7 surface and subsequently annealed at 870 K for 6 min. The morphology and geometric structure of this phase have been studied by STM, LEED and RHEED. Its electronic structure has been studied by a combination of ARPES and density functional theory calculations. $USi_{1.67}$, with a hexagonal C-32 type structure was thought by Kanfmann [16] to be deficient in silicon, and was then shown by Brown [17] to be $USi_{1.67}$. This is the first time that this structure is obtained by solid-state epitaxy.

2. Experimental and theoretical details

The sample preparations and film growth were performed in several ultra-high vacuum (UHV) chambers. These chambers are connected using a radial distribution chamber with a base pressure of 5×10^{-10} mbar. The substrates were cut from n-type Si (1 1 1) wafers, and before being transferred into the UHV chamber, they were rinsed with boiled water, acetone and distilled water for

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several times. For the preparation of well-ordered and clean Si (1 1 1) − 7 × 7 surface, the sample was outgassed over night by direct current heating at a temperature of ~600 °C, and then it was flashed up to 1200 °C for 8 s with vacuum not more than 3×10^{-10} mbar, and cooled to 950 °C very quickly and cooled down to room temperature at a rate of about 2 °C per second. After a long time outgassing of the uranium metal source (purity 99.9%), U was deposited onto the clean and well-ordered Si (1 1 1) − 7 × 7 surface at room temperature from an e-beam evaporator with a tungsten crucible. The deposition rate of U was estimated using STM by depositing sub-monolayer U on clean Au (1 1 1) surface. The base pressure was 5.8×10^{-11} mbar and vacuum did not rise above 3×10^{-10} mbar during evaporation. RHEED patterns were obtained with a 25 keV electron beam under a 1° or 2° incidence.

STM studies were conducted in another chamber with a base pressure less than 5×10^{-11} mbar, and during annealing of the films vacuum was not more than 4×10^{-10} mbar. All STM experiments were performed at LN_2 temperature (77 K). Tungsten tips were electrochemically etched and cleaned by high-temperature annealing in UHV conditions. All topographic images were recorded in the constant current mode. Photoemission studies were conducted in another chamber with a base pressure less than 7×10^{-11} mbar, where a hemispherical electron analyzer (VG – Scienta R4000) is fitted. A He discharge lamp with a toroidal monochromator was used for ultraviolet photoelectron spectroscopy. The overall energy and angular resolutions were set at 10–50 meV and 1°, respectively. The pass energy was set to 5 eV and the entrance slit to 0.5 mm.

Our total-energy calculations are carried out by employing the plane-wave basis pseudopotential method as implemented in the Vienna ab initio simulation package (VASP) [18]. The exchange and correlation effects are described with the GGA approximation in the Perdew–Burke–Ernzerhof (PBE) form [19–21]. The projected augmented wave (PAW) method of Blöch [21] is employed with the frozen-core approximation. Electron wave function is expanded in plane waves up to a cutoff energy of 400 eV and the lattice of hexagonal $USi_{1.67}$ is fully relaxed until the Hellmann–Feynman forces on each atom are less than 0.01 eV/Å. A 11 × 11 × 15 Monkhorst–Pack [22] k-point mesh is employed for integration over the Brillouin zone. The uranium $6s^26p^65f^36d^17s^2$ and silicon $3s^23p^2$ electrons are treated as valence electrons. 3 × 1 × 1 supercell was used for the band structure calculation of $USi_{1.67}$. Noncollinear calculations are used when considering the spin orbital coupling effects. The strong on-site Coulomb repulsions among the localized uranium 5f electrons are described by using the formalism formulated by Dudarev et al. [23–25]. In this scheme, the total GGA energy functional is in the form

$$E_{GGA+U}=E_{GGA}+\frac{U-J}{2}\sum_{\sigma}[Tr\rho^{\sigma}-Tr(\rho^{\sigma}\rho^{\sigma})] \quad (1)$$

where ρ^{σ} is the density matrix of f states with spin σ, while U and J are the spherically averaged screened Coulomb energy and the exchange energy, respectively. In this paper, the Coulomb U is treated as a variable, while the exchange energy is set to be a constant, J=0.51 eV. This value of J is in the ball park of the commonly accepted one for uranium compounds [26] and close to the theoretically predicted value of 0.54 eV in UO_2 [27]. Since only the difference between U and J is significant, we will henceforth label them as one single parameter $U_{eff}=U-J$, while keeping in mind that the nonzero J has been used during calculations. In this paper, U_{eff}=1 eV leads to the best agreement between the data observed experimentally and theoretical calculation.

3. Results and discussion

Deposition of 3 ML U on Si (1 1 1) − 7 × 7 surface and subsequently annealed at 870 K leads to the appearance of sharp hexagonal LEED patterns, as is shown in the inset of Fig. 1a, which indicates that crystalline film may have been formed. Fig. 1a shows STM topographic image of the formed new phase, and the majority of the surface shows layered structures with a substantial population of darker holes. There are many triangular and hexagonal islands and holes, and this phenomenon is consistent with the hexagonal LEED pattern. Fig. 1b shows profile along lines aa′ in Fig. 1a, and two typical step heights can be observed: around 2.0 Å and 4.0 Å high. The height of 4.0 Å corresponds to the c lattice parameter of the $USi_{1.67}$ structure (4.069 Å), and can be understood as a silicide step, while the step height of 2.0 Å was nearly half of the silicide step. The STM topographic image does not present changes with the voltage, making it possible to obtain STM images at very low gap voltages. This supports a metallic character of the surface layer, which can also be verified in the following valence band spectrum results. The main topographic features present on the uranium silicide p (1 × 1) surface are different from that of 2D $RESi_2$ surface. The latter shows large and flat terraces with an important number of triangular shaped holes and irregular clusters [1].

In our previous works, RHEED was used to investigate the lattice constants of this new phase, and compared with clean Si (1 1 1) [28]. It was found that their streak spacing is the same,

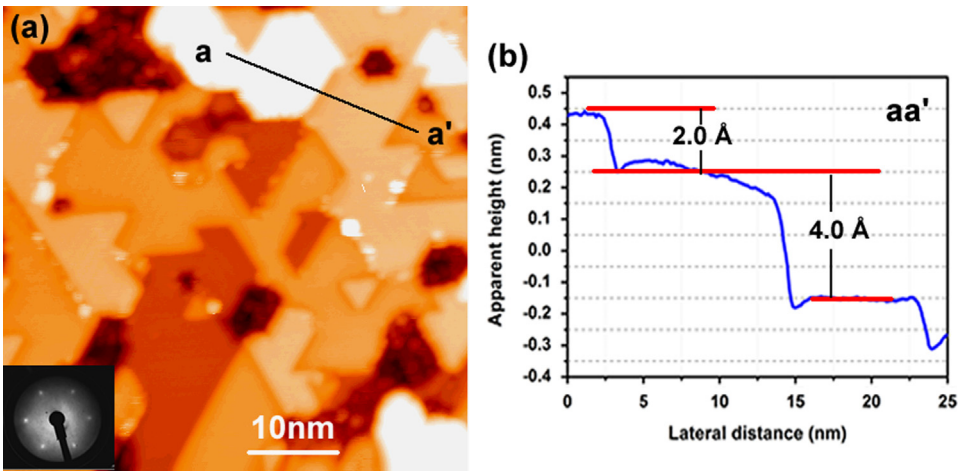

Fig. 1. (a) STM images of $USi_{1.67}$ film. Scanned area = 50 × 50 nm², V_g=1 V, and I_t=80 pA; the inset is LEED pattern of the $USi_{1.67}$ phase, E=63.5 eV and (b) line profile of aa′ in Fig. 1a.