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Hydrogen sorption sites in holmium silicide on silicon(1 1 1)

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The hydrogen sorption sites on the surface of holmium silicide grown on Si(1 1 1) have been determined using metastable de-excitation spectroscopy, ultraviolet photoemission spectroscopy and density functional theory calculations. Comparison of calculated and measured surface density of states spectra allow us to locate the position of the second subsurface hydrogen atom in each unit cell to an interstitial site in the layer of rare earth atoms. The hydrogenation energies indicate a reaction pathway that involves concomitant site occupation.

1. Introduction

The interaction of hydrogen with surfaces is of fundamental interest because it is the most basic adsorbate and acts as a prototype for understanding more complex chemisorption phenomena. An understanding of hydrogen storage in fuel cells is completely reliant on these processes [1]. Silicon device fabrication is also affected by the presence of hydrogen [2].

In this work we are concerned with the interaction of hydrogen with silicides of the rare earth metals grown on the Si(1 1 1) surface. Rare-earth silicides are of great interest due to the properties they exhibit as metal/semiconductor interfaces in a number of materials systems including heterostructures [3], nanowires [4], and sensors [5]. Depending on the amount of RE deposited, either a 2D or 3D silicide may form with the atomic structure of each shown schematically in Fig. 1. In both cases the surface of the silicide consists of a buckled Si bilayer that sits above a flat RE layer. The 3D silicide then has further, alternating layers of graphite-like Si and RE atoms with a network of vacancies distributed throughout the flat Si layers to relieve strain. This leads to a $\left(\sqrt{3}\times\sqrt{3}\right)R30^\circ$ stoichiometry with 1 in every 6 Si atoms missing.

The interaction of hydrogen with the 2D and 3D RE silicides on Si(1 1 1) results in fundamental changes to the surface structure and the electronic properties. H adsorption onto a 2D RE silicide results in a transition from a semimetal to a semiconductor [6]. The resulting passivation of the 2D $HoSi_2$ surface has also been investigated as a base for further overlayer growth [7]. Structurally, hydrogenation causes the surface bilayer to flip from type B in which the buckling direction is opposite that of the bulk to type A where they are equivalent [8]. This adsorption results in the interlayer spacing between the top Si bilayer and the flat RE layer expanding by 0.32 Å. In the 3D RE silicides H is known to bond to the top bilayer and to interstitial sites as in the 2D silicides but it has also been suggested that there is additional H passivation of dangling bonds in the vacancy network [9].

To determine the hydrogenation sites in the 2D RE silicides the electronic density of states (DOS) has been calculated with the extended Hückel method and compared with angle-resolved photoemission spectroscopy (ARPES) data [10]. This work suggests that two H atoms are chemisorbed into each unit cell in the 2D silicides, one bonding atop the silicon bilayer to the dangling bonds protruding into the vacuum and the other to interstitial sites in the RE hexagonal layer. It is not known definitively which site is occupied by this second, absorbed, H atom. The authors remark that from their ARPES data they could only 'tentatively assign' a band to the Er–H interstitial bonds. The Hückel model calculations indicate which of the interstitial sites has the larger hydrogenation energy and a comparison of calculated and measured band structures adds further evidence as to which interstitial site is occupied. However, there are problems with this method. The structures were not geometry optimised and the structural parameters were assumed using reasonable values extrapolated from experiment. In our experience non-optimised atomic positions can raise the energy of a model structure by more than 1 eV. Also, a complete range of possible model structures was not covered. The authors themselves remarked that the work could be extended by looking at more models with more precise ab initio techniques.

The aims of the density functional theory (DFT) calculations in this work are to provide a more accurate and complete survey of this system and to directly compare it with an experimental technique that has sufficient surface sensitivity to unambiguously determine the second hydrogenation site. In a recent paper [11] we have demonstrated how metastable de-excitation spectroscopy

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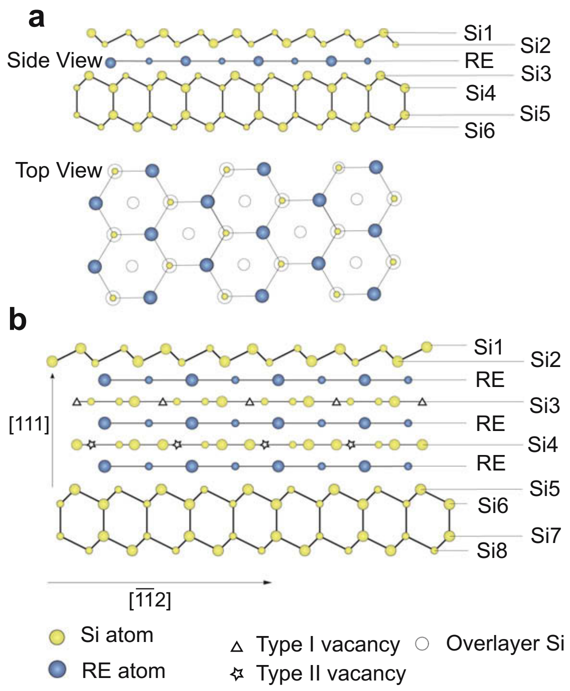

Fig. 1. A structural model of (a) 2D and (b) 3D RE silicides.

(MDS) and density functional theory produce directly comparable spectra that allow one to directly relate atomic structure to electronic properties. Such is the extreme surface sensitivity of MDS that for clean 2D holmium silicide we were able to depth resolve the different features in the MDS spectrum and show how sensitive these are to small changes in the rumpling amplitude of the outer silicon bilayer. In this work we apply this methodology to the hydrogenated RE silicides on Si(1 1 1). Key questions that we aim to answer are; what hydrogenation sites are occupied in this system? What are the reaction pathways to the formation of the hydrogenated surface? What changes occur to the surface atomic and electronic structure?

2. Experimental

Sample preparation was conducted in a vacuum chamber with a base pressure of 3×10^{-10} mbar and equipped with low-energy electron diffraction (LEED), ultraviolet photoemission spectroscopy (UPS), and MDS. Whilst the MDS apparatus has been described elsewhere [12], a brief overview is provided here.

Metastable (2^3S) He is produced in a hollow, cold-cathode dc discharge source. This supersonically expands through a small aperture into a high-vacuum beamline where laser cooling using light tuned to the resonance frequency of the 2^3S_1–2^3P_2 He transition collimates the He along the beamline axis. This process increases the intensity and purity of the beam as UV photons and 2^1S He atoms are not collimated and so continue to diverge. From the beamline, the He 2^3S atoms enter the sample chamber through an aperture and impinge on the sample at 45° to the surface normal. The collimation process leads to an intensity of the order of 10^{12} He 2^3S atoms s^{-1} cm^{-2} at the sample.

When conducting UPS, He I resonance photons ($h\nu = 21.22$ eV) were produced using an Omicron HIS 13 VUV He discharge source and as with MDS, were incident on the sample at 45° to the surface normal. The electron energy spectra for both MDS and UPS were measured at normal emission by an Omicron Vakuumphysik GmbH EA125 hemispherical analyser.

Si(1 1 1) substrates were cut from a lightly-doped, n-type wafer. These were cleaned by direct current heating to $\sim$1200 °C (as measured on an IR pyrometer) followed by a slow cool. The LEED pattern was then checked to ensure a 7 × 7 reconstruction.

Holmium was deposited onto a room-temperature substrate by direct current heating a Ta boat containing a Ho ingot, with deposition rates calibrated using a quartz crystal oscillator. During deposition, the chamber pressure did not rise above 1.0×10^{-9} mbar. The sample was annealed for 10 min at approximately 500 °C after deposition to achieve the silicide structure. The Ho coverages quoted in this paper are nominal, and may differ in reality due to island formation across parts of the surface as is known to happen with 3D RE silicides.

The samples were then passivated with H. This was done by introducing $\sim3.5\times10^{-6}$ mbar of H_2 into the system for 15 min with the sample at room temperature. H_2 was cracked to form monatomic H using a tungsten filament situated directly in front of the sample at a distance of approximately 50 mm. The LEED pattern was checked to confirm spot reversal which indicates complete H termination. MDS and UPS were then conducted.

After H termination of the surface, the 2D silicide had a $p(1\times1)$ LEED pattern, although the threefold symmetry was reversed compared to the clean silicide which indicates a switch in the surface buckling direction from B-type to A-type [13]. For the 3D surface, the $\left(\sqrt{3}\times\sqrt{3}\right)R30^\circ$ LEED pattern remained after hydrogenation and the same switch in the threefold symmetry was again observed. If the hydrogenated 2D surface was heated to around 400 °C the H largely disassociated from the surface, evidenced by a re-reversal of the threefold symmetry indicating a flip of the top bilayer back to B-type, although the symmetry reversal was not perfect and the LEED pattern showed strong hints of sixfold character suggesting not all of the H disassociated in this way. Other studies have also observed this process [9].

Fig. 2 shows the UPS spectra for all Ho coverages after H termination. The spectrum for Si(1 1 1)-1 × 1–H is provided for reference. The surface and bulk density of states for Si(1 1 1)-1 × 1–H have previously been calculated by Pandey which show a large drawn out feature from the bulk between approximately −2 eV and −4 eV [14]. This same feature is visible in the UPS spectrum for Si(1 1 1)–H at the same energy range. A UPS peak at −6.5 eV corresponds to a small, local maximum in the SDOS.

On the H terminated silicide surfaces, the feature labelled *a* in the spectra is at a similar energy to a feature observed previously

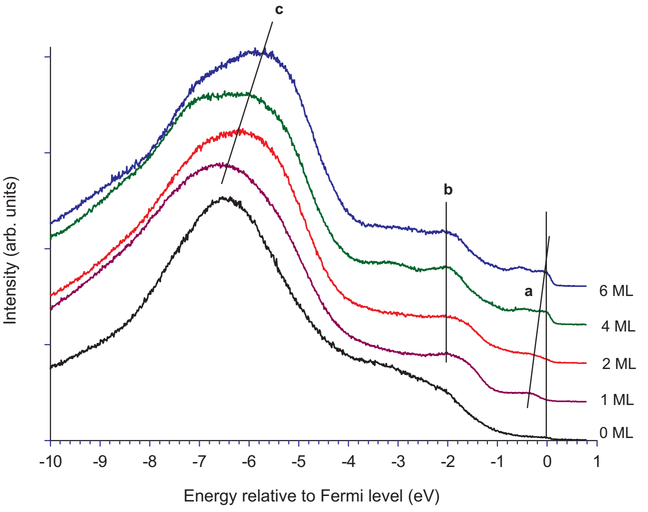

Fig. 2. UPS spectra as a function of Ho coverage for H terminated Ho silicide surfaces. Spectra have been normalised and offset for clarity.