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Single layer nickel disilicide on surface and as embedded layer

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Abstract. Single monolayers of various materials (e.g. graphene, silicene, bismuthene, plumbene, etc) have recently become fascinating and promising objects in modern condensed-matter physics and nanotechnology. However, growing a monolayer of non-layered material is still challenging. In the present report, it will be shown that single monolayer $NiSi_2$ can be fabricated at Si(111) surface stabilized by either Tl, Pb or In monolayers. Nickel atoms were found to intercalate the stabilizing metal layers upon deposition and to reside in the interstitial sites inside the first silicon bilayer of bulk-like-terminated Si(111)1×1 surface. The interstitial positions almost coincide with the bulk $NiSi_2$ atomic positions thus forming $NiSi_2$ single layer. Atomic and electronic structure of formed systems is described in detail by means of a set of experimental techniques, including low-energy electron diffraction, scanning tunneling microscopy, angle-resolved photoemission spectroscopy and also first-principles density-functional-theory calculations. Quality of formed single monolayer $NiSi_2$ was additionally confirmed by *in situ* four-probe transport measurements that show that single monolayer $NiSi_2$ preserves a metallic-type conductivity down to 2.0 K. Moreover it was found that delta-type structure with atomic sheet of $NiSi_2$ silicide embedded into a crystalline Si matrix can be fabricated using room-temperature overgrowth of a Si film onto the Tl stabilized $NiSi_2$ surface layer. Confinement of the $NiSi_2$ layer to a single atomic plane has been directly confirmed by high-resolution transmission electron microscopy.

1. Introduction

Among transition metal silicides, $NiSi_2$ has exceptional fluorite structure (along only with $CoSi_2$) with remarkably close lattice matching to crystal silicon, such that it displays perfect epitaxial growth on Si surfaces with an atomically abrupt interface [1, 2]. More importantly, nickel disilicide is a 'good' metal and known to be metallic down to 1 K [3]. In 1983, Tung et al [1] showed that $NiSi_2$ layers can be grown epitaxially on Si(111) and Si(100) surfaces, which has generated considerable interest in the subject due to its importance for semiconductor microelectronics. In subsequent years the formation process of epitaxial $NiSi_2$ layers on silicon surface has been studied and it was shown that thick $NiSi_2$ films can be controllably formed in two possible orientations [2]: type-A (Si lattice planes continue through the interface) and type-B (180° rotated). However, it was also shown that single or double monolayer $NiSi_2$ cannot be formed [4]. Its formation remains a desirable task because single monolayers of various materials (e.g. graphene, silicine, bismuthene, plumbene, etc) have recently become fascinating and promising objects in modern condensed-matter physics and nanotechnology. At the same time, growing a monolayer of non-layered material is still challenging.

2. Results and discussions

Figure 1 illustrates the growth procedure that was used to fabricate a single monolayer nickel disilicide. In the first step, Tl/Si(111)1×1 surface was prepared (figure 1(a)), which is known to contain 1.0 ML of Tl atoms occupying every T_4 site on the bulk-like-terminated Si(111) surface (fig.2 (a)). To form the $NiSi_2$ layer, nickel was deposited onto the Tl/Si(111) surface with postannealing at 300°C. As it was proven by angle-resolved photoemission spectroscopy and first-principles density-functional-theory calculations, adsorbed Ni atoms penetrate through the Tl layer to form $NiSi_2$ monolayer sheet beneath it [5].

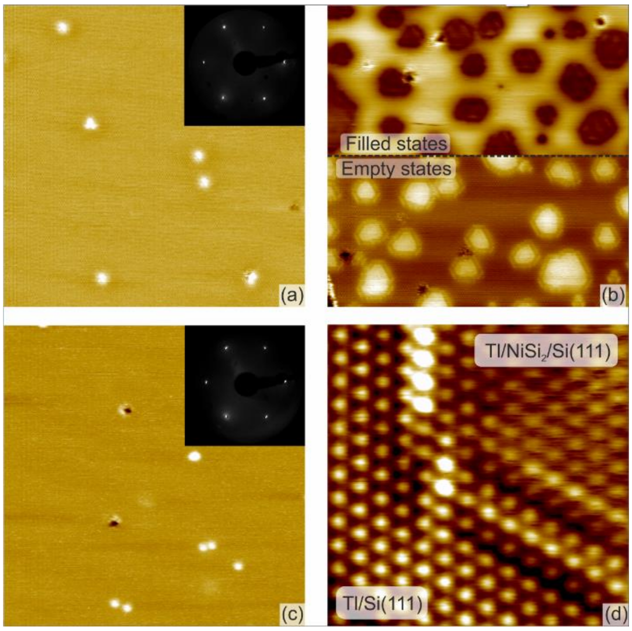

Fig. 1. *Formation of the Tl/NiSi₂/Si(111) system. 50×50 nm² STM images of (a) the initial Tl/Si(111) surface (empty states), (b) the surface at the intermediate stage with 0.2 ML of Ni deposited onto Tl/Si(111) surface at RT followed by 300°C annealing; (c) final Tl/NiSi₂/Si(111) surface with 1.0 ML of Ni deposited (filled states). The upper inserts in (a) and (c) show corresponding LEED patterns (E_p = 54 eV). (c) - 5 × 5 nm² high-resolution STM image of the border area between Tl/NiSi₂/Si(111) and Tl/Si(111).*

Figure 1(b) illustrates the intermediate stage, when about 0.2 ML of Ni was deposited and the surface contains patches of Tl/$NiSi_2$/Si(111) surrounded by areas of Tl/Si(111). A high-resolution STM image shown at figure 1(d) demonstrates border area between Tl/$NiSi_2$/Si(111) and Tl/Si(111). When 1.0 ML of Ni is deposited followed by annealing at 300°C, a homogeneous highly-ordered Tl/$NiSi_2$/Si(111) surface forms (fig. 1(d)). The same formation routine can be used with Pb [6] and In monolayers as stabilizers of $NiSi_2$ layer.

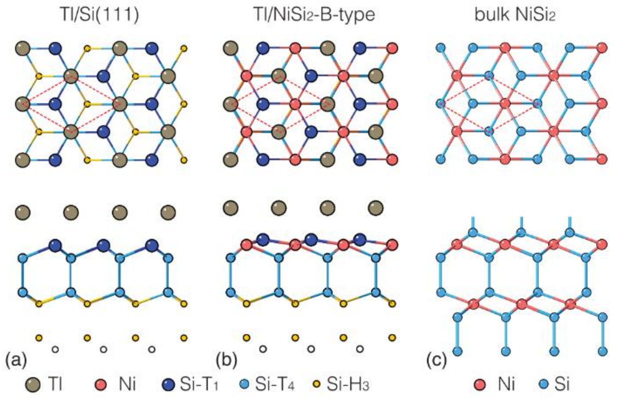

Fig. 2. *Atomic ball-and-stick models of (a) initial Tl/Si(111) surface, (b) Tl/NiSi₂/Si(111) surface and (c) NiSi₂ bulk crystal. Tl atoms are shown by gray balls, Ni atoms by red balls and Si atoms by balls and circles of different sizes and colors (dark blue, light blue, yellow and white) depending on the site and atomic layer. The 1×1 unit cells are outlined by dashed red rhombuses.*

Nickel atoms were found to intercalate Tl layer upon deposition and to reside in the interstitial sites inside the first silicon bilayer of bulk-like-terminated Si(111)1×1 surface (fig.2 (b)). The interstitial positions almost coincide with the bulk $NiSi_2$ atomic positions thus forming $NiSi_2$ single layer (fig.2 (c)).

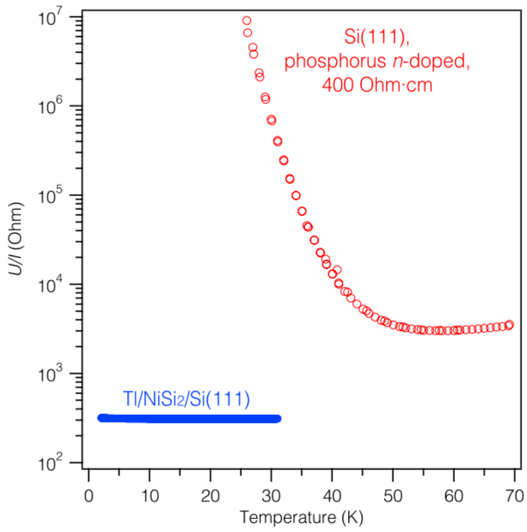

Fig. 3. *Temperature dependence of sheet resistance of the Tl/NiSi₂/Si(111) sample (blue diamonds) in comparison with that of the bare Si(111) substrate (red circles).*

Angle-resolved photoemission spectroscopy show that formation of $NiSi_2$ single layer enhance metallicity of the surface regardless of the stabilizing element (Tl, Pb or In). Metallic character was also confirmed by the *in situ* transport measurements with four-point-probe technique, whose results are presented in figure 3. It can be seen that in contrast to the bare Si(111) substrate, the Tl/$NiSi_2$/Si(111) sample demonstrates a metallic-type conductivity down to 2.0 K.

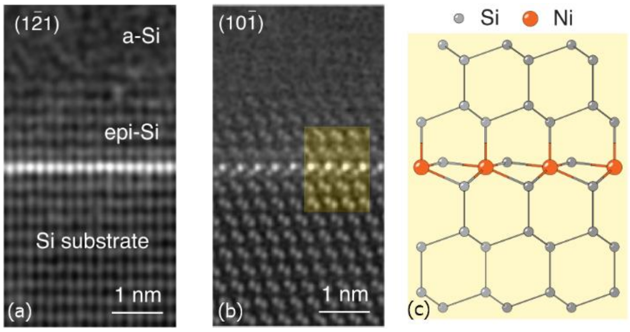

Fig. 4. *High-resolution transmission electron microscopy characterization of the formed Si/NiSi₂/Si(111) delta-structure: (a) - (12$\bar{1}$) cut cross-section sample, (b) - (10$\bar{1}$) cut cross-section sample. (c) - ball-and-stick model of the NiSi₂ delta-layer.*

Finally room temperature Si deposition onto Tl-stabilized surface monolayer $NiSi_2$ was found to facilitate formation of embedded by Si crystalline matrix monolayer $NiSi_2$, or in other words $NiSi_2$ delta layer in silicon [7]. Figure 4 contain high-resolution transmission electron microscopy images of two different cross-sections (a) and (b) of formed delta layer along with atomic model (c). Such $NiSi_2$ delta-layer demonstrates advanced values of conductivity and carrier mobility (as was shown by *ex situ* low-temperature conductivity and Hall measurements) and highly stable in air making it almost ideal model system for exploring transport through a single-atomic-layer metal.

4. Conclusions

Single layer $NiSi_2$ was fabricated on Si(111) surface and as embedded delta-type layer inside Si crystal matrix for the first time. Tl, In or Pb monolayers were essential elements required for its formation and stabilization. *Ex situ* and *in situ* low-temperature conductivity measurements and angle-resolved photoemission spectroscopy show that single layer $NiSi_2$ exhibits metallic properties.

Acknowledgements

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