Nanoscale patterns in the mixed Pb and Tl atomic layer on $NiSi_2$/Si(111)

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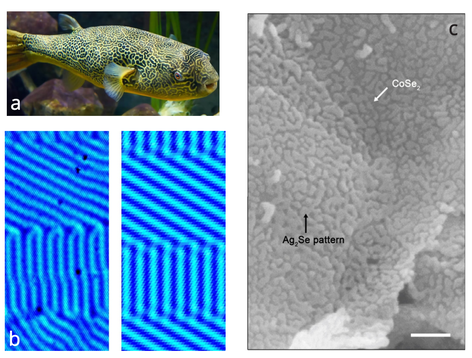
Introduction

The formation of two-dimensional (2D) metallic compounds based on heavy elements on different substrates sparked enormous interest not only due to the possibility of their existence but owing to unique properties which have been observed. Among them, 2D superconductivity [1], Rashba-type splitting of surface states [2] and quantum spin Hall effect [3] are of great interest from the viewpoint of further applications in new spintronics devices. Being the heaviest elements of III and IV groups, Tl and Pb contribute to strong spin-orbit coupling in surface structures, leading to the emergence of interesting properties [4].

In the present work, we report on the formation of nanoscale Turing-like patterns in the mixed Pb and Tl atomic layer which have been formed as a result of Pb atoms adsorption onto $NiSi_2$ sandwiched between Si(111) substrate and a capping Tl layer [5]. Electronic and atomic structures were studied using low-energy electron diffraction (LEED), scanning tunneling microscopy (STM), angle-resolved photoelectron spectroscopy (ARPES) and first-principles density-functional theory (DFT) calculations.

Alan Turing's patterns



Examples of Turing's patterns (a) in nature, (b) in Bi monolayer, (c) in Ag_2Se-$CoSe_2$

Ordered patterns can arise out of disorder during morphogenesis. An explanation for this puzzle was put forward by Turing, who explained the emergence of stationary patterns by invoking the interplay between an activator and an inhibitor with different diffusion rates. Moreover, their appearance strongly depends on starting conditions. Turing's theory of diffusion–reaction has proven to be extremely influential across many disciplines. For example, the pigment patterns on sea shells, stripes on tropical fish and the purely chemical system of chlorite–iodide–malonic acid have been studied as Turing patterns.

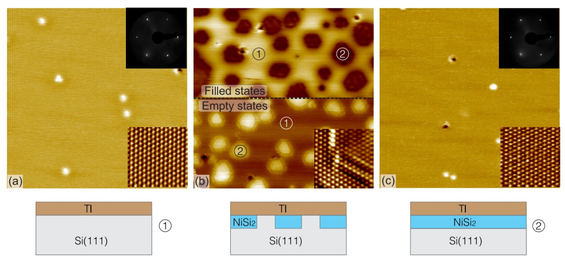
Having said that, despite the fact that in environment Turing's patterns are utterly widespread, in nanostructures they weren't observed except several cases [8, 9].

$$\frac{\partial u_a}{\partial t} = D_a \nabla^2 u_a + f_a(u_a, u_h),$$
$$\frac{\partial u_h}{\partial t} = D_h \nabla^2 u_h + f_h(u_a, u_h),$$

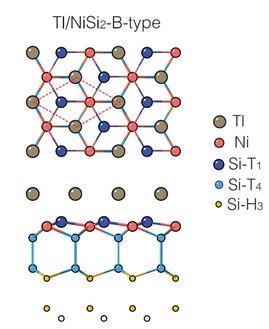
Properties of 2D heavy metals

Heavy metals on $NiSi_2$ substrate

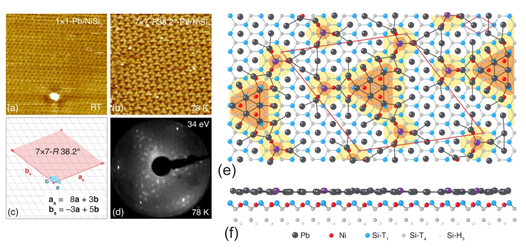
The growth of non-layered materials on different substrates is a perspective area of condensed matter science. However, the formation of non-layered materials is still challenging. In the recent article was reported about possibility to fabricate Tl monolayer on $NiSi_2$, where Tl was used as a surfactant and stabilizer [5]. The electronic band structure of the system is clearly metallic, and contains electron and hole pockets related to the Tl and $NiSi_2$ layers, respectively. The surface-state bands are spin-split due to the presence of a Tl layer with a strong spin–orbit coupling.



Formation of the Tl/$NiSi_2$/Si(111) system. 50×50 nm^2 STM images and corresponding schematics of (a) the initial Tl/Si(111) surface (empty states, +1.0 V, 0.4 nA), (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 (±0.5 V, 70 pA); (c) final Tl/$NiSi_2$/Si(111) surface with 1.0 ML of Ni deposited (filled states, −1.0 V, 0.4 nA). The upper inserts in (a) and (c) show corresponding LEED patterns (*Ep* = 54 eV). The lower insets show 5×5 nm^2 high-resolution STM images of the surfaces with that in (b) displaying the border area between Tl/$NiSi_2$/ Si(111) and Tl/Si(111) regions indicated in (b) as 2 and 1, respectively. STM images and LEED patterns were recorded at RT [5].



Atomic structure top view and side view [5]

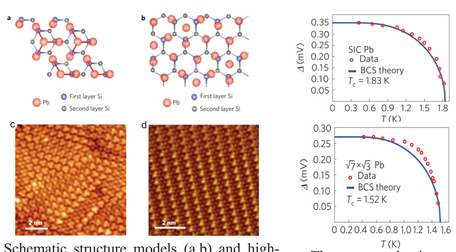


(a) Empty-state (2.5 V, 100 pA) 10×10 nm^2 STM image of the Pb/ $NiSi_2$/Si(111)1×1 surface acquired at RT. (b) Empty-state (+0.5 V, 500 pA) 40×40 nm^2 STM image of the Pb/$NiSi_2$/Si(111)7×7-R38.2 ° surface acquired at 78 K. (c) Schematics illustrating crystallography of the 7×7-R38.2° 2D lattice. The 1×1 and 7×7-R38.2 ° unit cells are shown by blue and pink rhombuses, respectively. (d) LEED pattern (*Ep*=34 eV) from the Pb/$NiSi_2$/Si (111)7×7-R38.2° surface at 78 K. (e) Top and (f) backside views of the ball-and-stick model of the Pb/ $NiSi_2$/Si(111)7 × 7-R38.2° structure with 55 Pb atoms per 7×7 unit cell. Pb atoms are shown by black balls, Ni atoms by red balls, Si atoms corresponding to the T_1, T_4 and H_3 adsorption sites are indicated by blue, light gray and white balls. The regions occupied by Pb atoms in the H_3-T_4 bridge sites and the T_1 sites are highlighted by yellow and orange colors, respectively [6].

The same situation was observed when instead of Tl monolayer Pb ML was used. At RT crystalline structure is the same, but when the system is cooled down (e.g., to 78 K), it converts into the long-periodic reconstructions having the 7×7 periodicity rotated with respect to main Si(111) directions by 38.2 ° [6].

Heavy metals on Si(111)

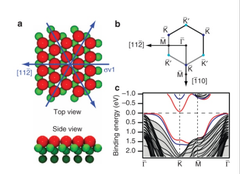
One-atomic layers of Pb and Tl atoms on Si(111) exhibit a plethora of intriguing properties. The Pb films undergoes superconducting transitions, while 1x1-Tl has full spin polarizations of valleys which is perspective for devices of spintronic.

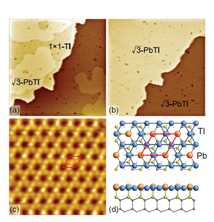


Schematic structure models (a,b) and high-resolution STM images (c, d) of the SIC-Pb (a,c), √7×√3-Pb (b,d) phases grown on Si(111) substrate [1].

The superconducting gap of the Pb phases as a function of temperature [1]

Basic properties of Tl/Si(111)-(1x1). (a) Atomic structure of the system. Red and green circles represent the Tl and Si atoms, respectively, and the blue arrows indicate the mirror planes. (b) The SBZ of Tl/Si(111)-(1x1). The symmetry points Kand K′ are indicated by dark-blue and light-blue circles. (c) Energy-band dispersions obtained by a relativistic first-principles band calculation. Red and blue lines are spin-polarized surface states [7].





One-Atom-Layer Tl-Pb Compound on Si(111) growth procedures (a-b), high resolution (5x5 nm^2) STM image (c) and atomic model (d)

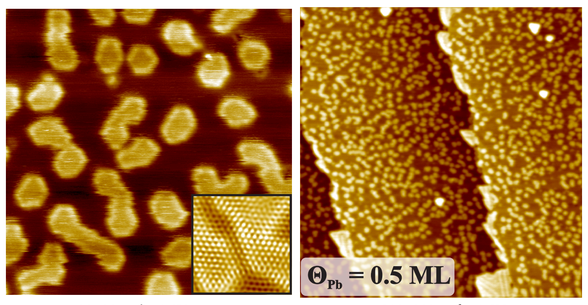
The 2D compound of 1 ML Tl with 1/3 ML Pb having √3×√3 periodicity on Si(111) appears to be a 2D material that combines together the giant Rashbatype spin splitting (~250 meV) with the superconductivity at a sizable transition temperature of 2.25 K followed by the Berezinskii-Kosterlitz-Thouless mechanism [4].

STM and LEED

Pattern formation via 1×1-Tl/$NiSi_2$

In the present work we evaporated Pb atoms onto Tl/$NiSi_2$ surface at RT. In contrast to the (Pb, Tl)/Si(111) system, where several compound surface reconstructions are formed, Pb and Tl atoms on the $NiSi_2$ monolayer are separated and create a mixture of discrete Pb/$NiSi_2$ and Tl/$NiSi_2$ structures.

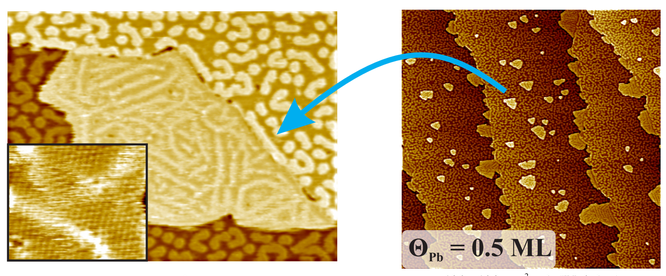
After adsorption of 0.5 ML at the surface, bright Pb segments of hexagonal form with 1x1 periodicity appeared as a result of the displacement of Tl atoms. Pb atoms can change their positions with Tl and, as a result, change their form.



20×20 nm^2, -1.5V
on the insert 5×5 nm^2, -1.5V

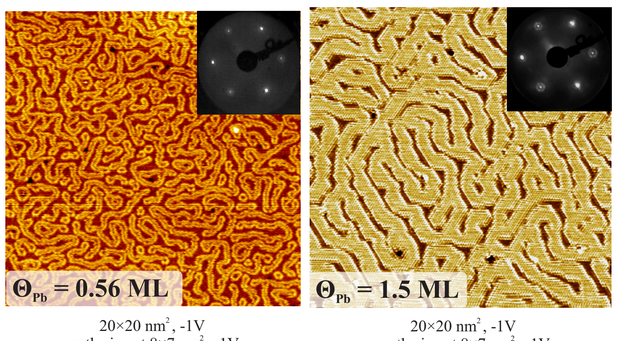
200×200 nm^2, -1.5V

Tl atoms which were dislodged, with a particular percentage of Pb (~10%), which doesn't contribute to the formation of the patterns, may form Moire 2D islands of double-layer height with 1x1 periodicity.



20×20 nm^2, -1V
on the insert 8×7 nm^2, -1.3V

400×400 nm^2, -1.5V, 0.1nA

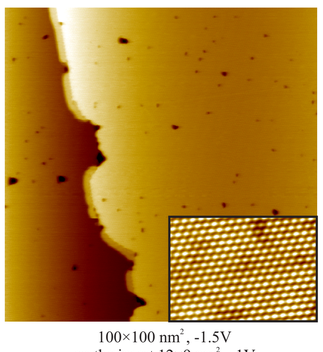


20×20 nm^2, -1V
on the insert 8×7 nm^2, -1V

20×20 nm^2, -1V
on the insert 8×7 nm^2, -1V

During the incrementation of Pb coverage, patterns changed their appearance from mainly separated hexagonal areas to long ribbons over the whole surface. In the meantime, LEED registrated the emergence of rings centered at the main reflexes. The radius of the rings about 0.28 nm^{-1} (7.14 nm) which corresponds to the middle wide of the ribbons. Moreover, ARPES indicated metallic bands of Pb/$NiSi_2$.

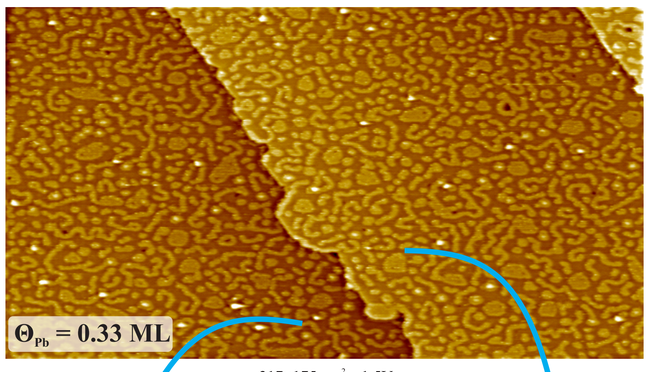
Pattern formation via √3×√3-(Pb, Tl)



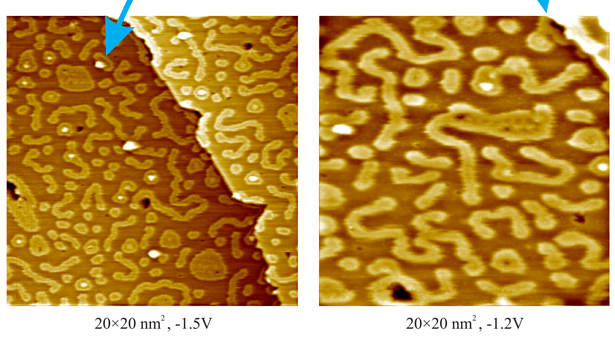
100×100 nm^2, -1.5V
on the insert 12×9 nm^2, -1V

With an intention to check how the appearance of patterns depends on starting conditions we grew the cilicide using √3×√3-(Pb, Tl) compound which has in its composition 1 ML Tl with 1/3 ML Pb,
as a surface for further adsorption of Ni atoms at RT with subsequent anneal at 300 °C.

As a result, ribbons changed significantly and became far longer and also large hexagonal-like areas emerged.

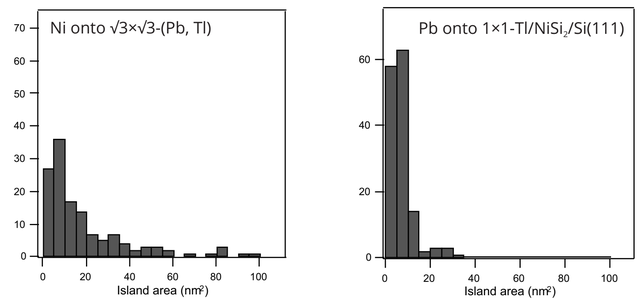


317×175 nm^2, -1.5V



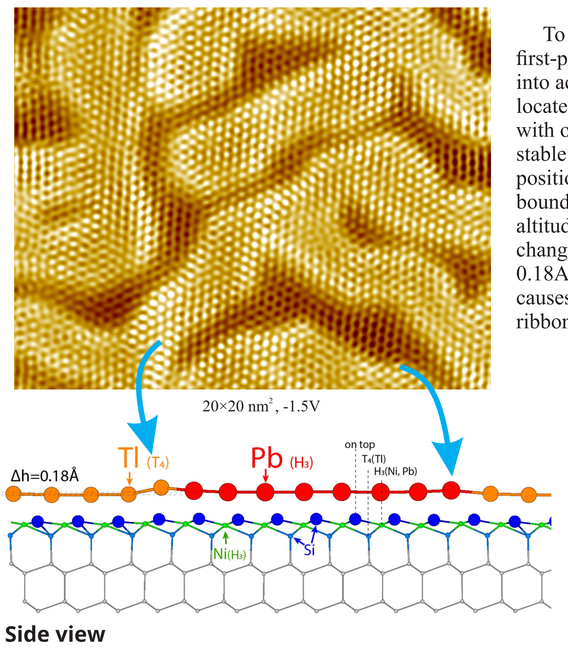
20×20 nm^2, -1.5V

20×20 nm^2, -1.2V



Area analysis revealed that compared to the initial procedure, evenly distribution changed to more drastic one where areas of about 60 nm^2 are privalent.

Structural model



To elucidate the atomic arrangement of the system, first-principle calculations have been performed taking into account the fact that both Pb and Tl atoms are located an the $NiSi_2$ layer and have 1x1 periodicity with one atom per unit cell. It was shown that the most stable configuration is when Tl atoms occupy T_4 positions and Pb H_3. Also, there are two types of boundaries which can be described by different altitudes of Tl atoms. At the first one Tl atoms slightly change their altitude compared to $TlNiSi_2$, by 0.18A,but at the second one don't. This difference causes different STM appearance of the patterns: each ribbons has a bright and dim boundaries.

Conclusion

A new two-dimensional compound has been found as a result of adsorption of Pb atoms at room temperature onto monolayer $NiSi_2$, which is sandwiched between Si(111) substrate and Tl capping layer. Pb atoms dislodge part of Tl and form the structure with the same 1×1periodicity but different STM contrast. In contrast to the (Pb, Tl)/Si(111) system, a phase separation takes place. Pb atoms agglomerate into compact nanoscale 2D islands separated by Tl layer. At higher Pb coverage, 2D islands merge into elongated ribbons of 7.14 nm width, which remind Turing patterns. At room temperature, Pb atoms can exchange their positions with Tl leading to constant movement of 2D islands and ribbons. Also, experiments revealed that the appearance of the patterns depends on starting conditions (initial surface). DFT calculations estimated that stable adsorption position for Tl and Pb atoms are T_4 and H_3, respectively.

Acknowledgement

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References

[1] T. Zhang, P. Cheng, W.-J. Li, Y.-J. Sun, G. Wang, X.-G. Zhu, K. He, L. Wang, X. Ma, X. Chen, Y. Wang, Y. Liu, H.-Q. Lin, J.-F. Jia, and Q.-K. Xue. Nat. Phys. 6, 104 (2010)

[2] K. Yaji, Y. Ohtsubo, S. Hatta, H. Okuyama, K. Miyamoto, T. Okuda, A. Kimura, H. Namatame, M. Taniguchi, and T. Aruga. Nat. Commun. 1, 17 (2010)

[3] C.-H. Hsu, Z.-Q. Huang, C.-Y. Lin, G. M. Macam, Y.-Z. Huang, D.-S. Lin, T. C. Chiang, H. Lin, F.-C. Chuang, and L. Huang. Phys.Rev.B 98, 121404(R) (2018).

[4] A. V. Matetskiy, S. Ichinokura, L. V. Bondarenko, A. Y. Tupchaya, D. V. Gruznev, A. V. Zotov, A. A. Saranin, R. Hobara, A. Takayama, and S. Hasegawa. Phys. Rev. Lett. 115, 147003.

[5] L.V. Bondarenko, A.Y. Tupchaya , A.N. Mihalyuk, S.V. Eremeev, A.V. Matetskiy, N.V. Denisov, Y. E. Vekovshinin, A.V. Slyshkin, D.V. Gruznev, A.V Zotov, A.A. Saranin. 2D Materials. 7 (2020) 025009.

[6] L.V. Bondarenko *et al.* Surface Science 716,121966 (2022)

[7] Sakamoto *et al.* Nature Communications 4, 2073 (2013).

[8] Xiao-Long Zhang+, Peng-Peng Yang+, Ya-Rong Zheng, Yu Duan, Shao-Jin Hu, Tao Ma, Fei-Yue Gao, Zhuang-Zhuang Niu, Zhi-Zheng Wu, Shuai Qin, Li-Ping Chi, Xingxing Yu, Rui Wu, Chao Gu, Cheng-Ming Wang, Xu-Sheng Zheng, Xiao Zheng, Jun-Fa Zhu, and Min-Rui Gao. Angewandte Chemie Vol. 60 (2021)

[9] Yuki Fuseya, Hiroyasu Katsuno, Kamran Behnia and Aharon Kapitulnik. Nat. Phys. 17 (2021)