*Solid State Phenomena Vol. 213 (2014) pp 65-70*
*© (2014) Trans Tech Publications, Switzerland*
*doi:10.4028/www.scientific.net/SSP.213.65*

# Sodium doping of Bi/Si(111) ultra-thin films

M.V. Ryzhkova[a,1*], D.V. Gruznev[1,2], E.A. Borisenko[1], D.A. Tsukanov[1,2]

[1] Institute of Automation and Control Processes, FEB RAS, 5 Radio St., Vladivostok 690041, Russia

[2] Far Eastern Federal University, 8 Sukhanova St., Vladivostok 690950, Russia

[a]e-mail: lavric@iacp.dvo.ru

**Keywords:** surface reconstructions, Si(111), bismuth, sodium, low energy electron diffraction, surface conductivity.

**Abstract.** Changes in electrical conductance of the Bi/Si(111) reconstructed surfaces and Bi{012} or Bi(001) ultra-thin films have been studied after sodium deposition at room temperature. It was observed that deposition of sodium onto Si(111)-β-√3×√3-Bi surface results in increasing of surface conductivity up to 0.3 monolayers (ML) of adsorbed sodium atoms. These conductance changes were explained by developing of the metallic surface states in the band gap as revealed by angle resolved photoemission spectroscopy spectra. Moreover, it was shown that sodium adsorption of 0.5 monolayers onto Bi{012} and Bi(001) thin films leads to drastic changes in its surface conductivity including a peak of maximum electrical conductance.

## Introduction

As was recently shown [1] a small amount of adsorbed sodium on the reconstructed Si(111)-α-√3×√3-Au surface at 300°C leads to significant changes in electronic and atomic structures. Angle resolved photoemission spectroscopy (ARPES) study demonstrated the formation of metallic surface states with a small effective mass of electrons. This result is well correlated with surface conductivity study that revealed the conductivity increasing in this case [2]. Due to similarity with doping of bulk semiconductors sodium atoms on the surface may be considered as dopants for the Si(111)-α-√3×√3-Au reconstruction.

Last time surfaces with bismuth components, for example, Si(111)-β-√3×√3-Bi reconstruction (hereafter β√3-Bi) or Bi(001) thin films have attracted attention due to their large Rashba spin splitting in the valence band [3]. But from the electronic structure study it is obvious that their surface electrical conductivity can not be high enough in comparison with the metallic reconstructed surfaces and ultrathin films such, for example, as Si(111)-*h*-√3×√3-(Au,Na) [4], Si(111)√21×√21-(Au,Ag) [5] and copper nanowires and films on the Si(111)5,55×5,55-Cu reconstructed surface [6]. Possibility for tuning the physical properties of Bi/Si(111) structures which can be achieved by electron doping during sodium adsorption has stimulated us to perform the experimental study of surface conductivity of these systems. In this work we have studied the sodium adsorption on the Si(111)√3-Bi surface and bismuth ultra-thin films by low energy electron diffraction (LEED), ARPES and *in situ* surface conductivity measurements.

## Experiment

The experiments were performed in two separate ultra-high-vacuum chambers with the base pressure in both in the ~$10^{-10}$ Torr range. The first chamber equipped with the ARPES and LEED facilities was used for studying the electronic structure of the surface. The electron spectrometer has energy resolution of about 35 meV. In the second chamber equipped with LEED and the four-point probe technique unit the changes in surface conductivity were measured at room temperature (RT).

The substrates were cut from standard *n*-type Si(111) wafers with resistivity 45 Ω·cm (size 15×5×0.45 $mm^2$). Atomically clean Si(111)7×7 surfaces were prepared in situ by flashing to 1280°C after first outgassing the samples at 600°C for several hours. The temperature of the sample was controlled both with an optical pyrometer and by the resistivity value.

Atomic sodium was deposited from SAES Getters S.A. source at a rate 1/3 ML/min. The sodium coverage was calibrated by the formation of Si(111)3×1-Na surface reconstruction [7,8] and position of metal–to-insulator transition after sodium deposition onto Si(111)7×7 at RT [9] in conductance measurement process at a rate of 1/3 ML/min with accuracy of about 0.05 ML/min. Bismuth was evaporated from home-made Knudsen cell, and its amount was calibrated by formation of β√3-Bi surface phase at a rate of 1 ML/min [10].

## Results and discussions

It is known that β√3-Bi surface phase has a semiconductor electronic structure and demonstrating surface electrical conductance even lower than that for Si(111)7×7 one [3]. However, as revealed by surface conductance measurements, sodium deposition onto the β√3-Bi at RT results in increasing the electrical conductance until 0.3 ML of sodium (Fig. 1). At further deposition the electrical conductance slightly decreases and reaches a saturation level. The ARPES study shows that the sodium deposition produces appearance of the metallic surface states at M and K point (Fig. 2). It can be proposed that the atomic sodium donates its valence electron to the $\Sigma_1$ and $\Sigma_1'$ surface states thereby increasing its charge density. It results in significant changes in electronic structure and directly reflecting in the surface conductivity of this system due to a contribution of additional carriers. After 0.3 MLs of deposited sodium surface conductivity begins to fade and this decreasing in the conductance can be directly connected with scattering of charge carriers on the surface due to formation of metallic islands where excess sodium atoms are assembling [11]. In contradistinction to β√3-Bi phase sodium adsorption onto Si(111)-α-√3×√3-Bi (hereafter α√3-Bi) reconstructed surface with as well as onto Si(111)-s-√3×√3-Bi (hereafter s√3-Bi) surface has no significant influence on the surface conductivity because density of states in $\Sigma_1$ is negligible to contribute in electronic transport due to lower concentration of bismuth in these surface phases (1 ML of bismuth in β√3-Bi phase and 1/3 ML in α√3-Bi and s√3-Bi phases [10]).

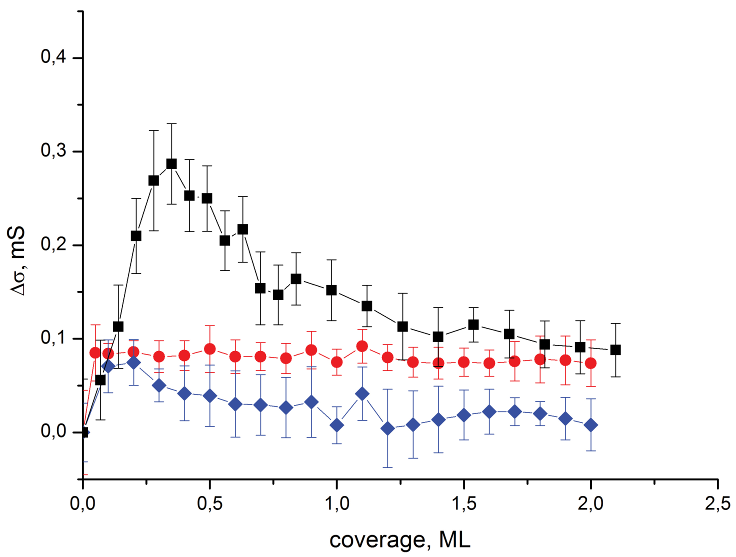


***Fig. 1*** *Changes in electrical conductance at Na adsorption onto the Si(111)-β-√3x√3-Bi (■), Si(111)-s-√3x√3-Bi (●) and Si(111)-α-√3x√3-Bi(♦) surface reconstructions at room temperature.*

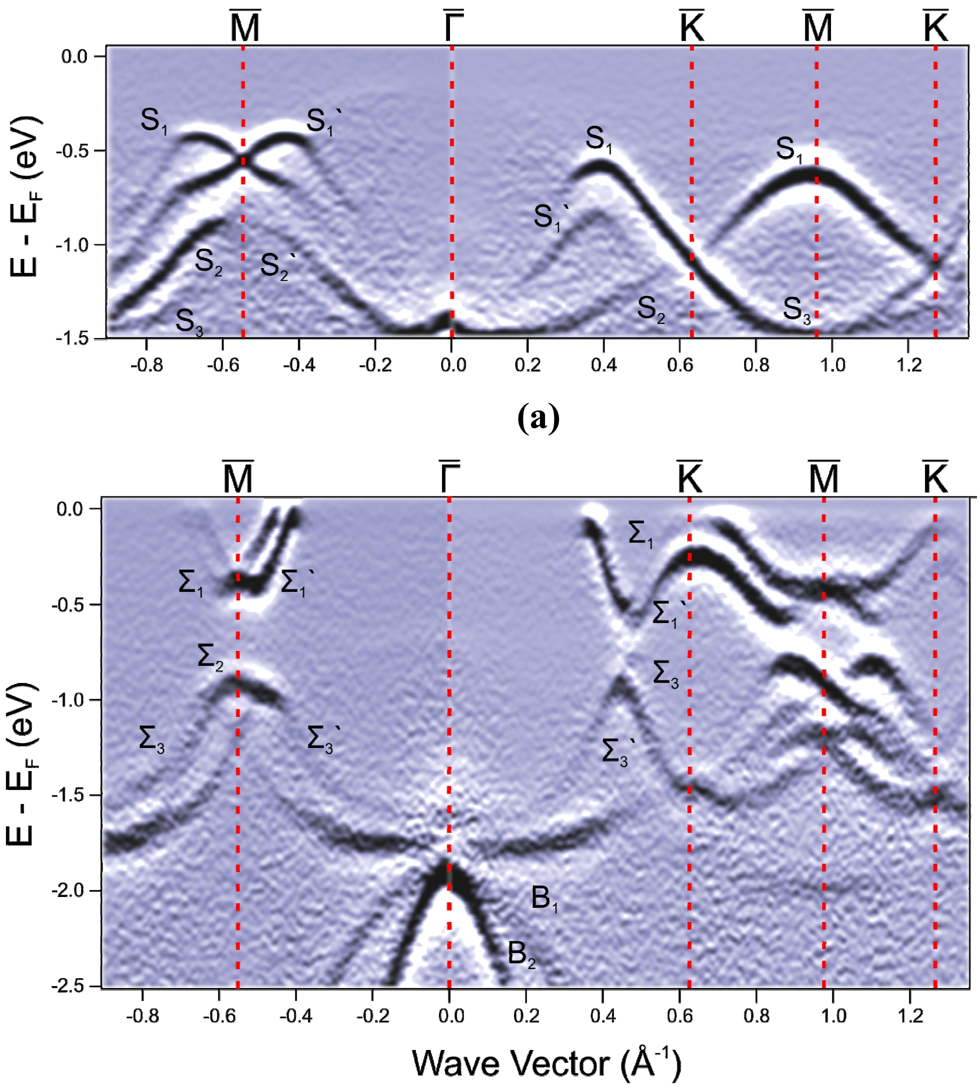


***Fig. 2*** *Changes in electronic structure (a) before and (b) after sodium adsorption onto the Si(111)-β-√3x√3-Bi surface reconstruction.*

As well as β√3-Bi surface reconstruction, Bi/Si(111) ultra-thin layers are known to have surface states that significantly modify physical properties of such films [3]. It is known that bismuth grows on the Si(111)7×7 surface by layer-by-layer mode, but the first layer is a strained structure of Bi{012}. At further bismuth adsorption at RT the film grows with Bi(001) orientation in accordance with hexagonal indexing [9]. As revealed by surface conductance measurements, deposition of sodium onto thin Bi(001) films results in a peak in electrical conductance at about 0.5 ML of sodium atoms (Figs 3 and 4). In Fig. 3 changes in the LEED patterns during sodium adsorption on the Bi{012} are shown. The maximum of conductance takes place at diffraction pattern c on Fig.2. Fig. 3a shows a 1×1 periodicity of Bi{012} with circle which corresponds to a multi-domain Bi{012} surface.

During sodium deposition diffraction patterns change drastically. The circle of smaller diameter appears, but the circle of polycrystalline Bi{012} film disappears (Fig. 3b). Fig. 3c shows Bi{012} structure and 1×1 periodicity with a unit vector of reverse lattice on ~28% smaller than the Bi{012} film's one. This diffraction pattern corresponds to a maximum of electrical conductance.

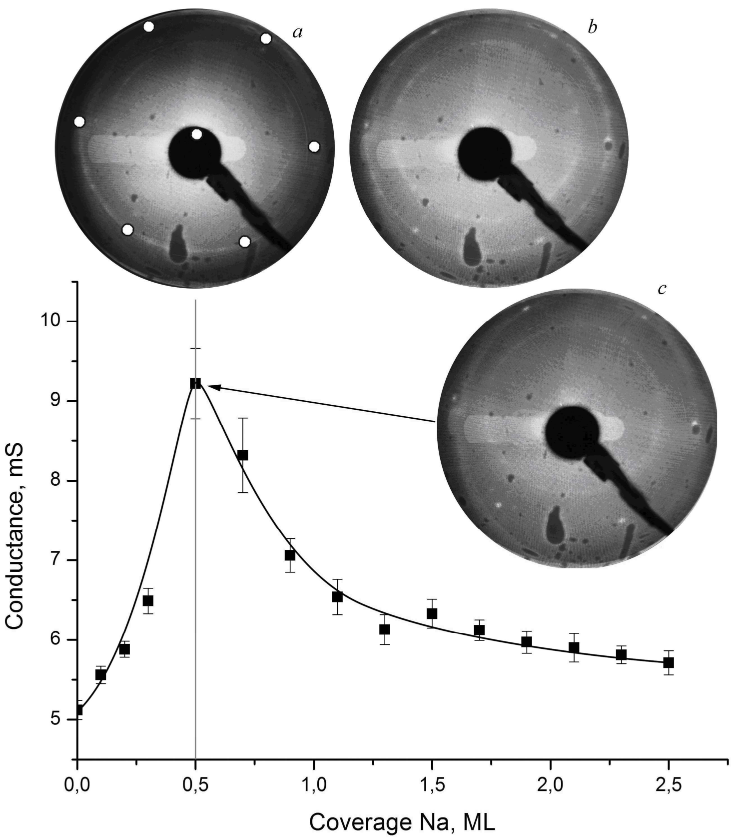


***Fig. 3*** *Changes in electrical conductance and LEED diffraction patterns at Na adsorption on Bi{012}. LEED patterns were taken at 50 eV.*

Fig. 4 shows the changes in surface conductivity and series of diffraction patterns after sodium deposition onto the Bi(001) films preliminary formed by bismuth adsorption of 20 MLs. Fig. 4a shows a 1×1 periodicity of Bi(001) with circle which corresponds to multi-domain Bi(001) surface oriented in different directions. After sodium deposition the diffraction pattern changes drastically. Fig. 4c shows Bi(001) structure and 1×1 periodicity with a unit vector of reverse lattice on ~14% larger than that of the bismuth (001) film's one. This diffraction pattern corresponds to maximum of electrical conductance. It means that at maximum conductance the Bi/Si(111) surface has a good crystallinity with two subsystems of bismuth domains.

The behavior of surface conductivity in the case of sodium deposition onto Bi{012} and Bi(001) surfaces looks similar to the case with that for β√3-Bi reconstructed surface. As well known [9] bismuth films are characterized by formation of surface states that significantly changes the properties of such films. From one hand bismuth is semimetal with poor conductance but on the other hand its surface has metallic states with spin polarization. As we propose, although this will require further study, sodium atoms are able to donate its electrons to the surface states of bismuth film as well as in the β√3-Bi case. As result, surface conductivity during the sodium adsorption begins to increase until these surface states are enriched by arriving carriers. After surface states are saturated, excess sodium atoms form ionized impurities that are serve as scattering centers for carriers leading to decreasing in surface conductance.

**Conclusions**

Changes in surface electrical conductance of Si(111)-β-√3×√3-Bi surface phase and Bi{012} or Bi(001) thin films have been studied after deposition of sodium atoms. Deposition of sodium onto Si(111)-β-√3×√3-Bi surface reconstruction has been reason of increasing in a conductance up to 0.3 ML of sodium dose. Conductance changes were explained by appearance of metallic surface states shown in ARPES study. Adsorption of sodium onto the Bi{012} and Bi(001) ultrathin films results in peak of electrical conductivity with maximum at 0.5 ML sodium coverage.

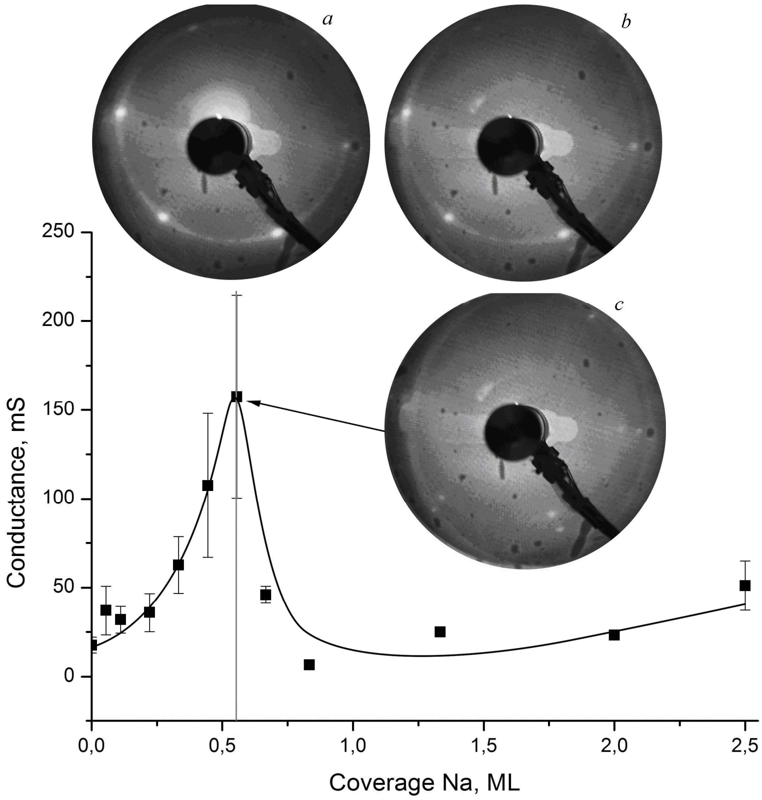


***Fig. 4*** *Changes in electrical conductance and LEED diffraction patterns at Na adsorption on Bi(001). LEED patterns were taken at 50 eV.*

**Acknowledgements**

This study was supported by the Russian Foundation for Basic Research (projects no. 12-02-31502, 13-02-00730).

**References**

[1] L.V. Bondarenko, D.V. Gruznev, A.A. Yakovlev, A.Y. Tupchaya, D. Usachov, O. Vilkov, A. Fedorov, D.V. Vyalikh, S.V. Eremeev, E.V. Chulkov, A.V. Zotov, A.A. Saranin, Sci. Reps. 3 (2013) 1826.

[2] D.A. Tsukanov, D.V. Gruznev, A.V. Zotov, A.A. Saranin, M.V. Ryzhkova, L.V. Bondarenko, E.A. Borisenko, in Physics, Chemistry and Application of Nanostructures, Proceedings of International Conference „Nanomeetings-2013“, World Scientific, Singapore (2013) 54.

[3] T. Hirahara, T. Nagao, I. Matsuda, G. Bihlmayer, E. V. Chulkov, Yu. M. Koroteev, S. Hasegawa, Phys. Rev. B 75 (2007) 035422.

[4] L.V. Bondarenko, A.V. Matetskiy, A.A. Yakovlev, A.Yu. Tupchaya, D.V. Gruznev, M.V. Ryzhkova, D.A. Tsukanov, E.A. Borisenko, E.N. Chukurov, D. Usachov, O. Vilkov, A. Federov, D.V. Vyalikh, A.V. Zotov, A.A. Saranin, “Effect of Na adsorption on structural and electronic properties of Si(111)√3×√3-Au surface” (to be published)

[5] D.A. Tsukanov, M.V. Ryzhkova, E.A. Borisenko, Semiconductors 47 (2013) 775.

[6] D.A. Tsukanov, M.V. Ryzhkova, D.V. Gruznev, O.A. Utas, V.G. Kotlyar, A.V. Zotov, A.A. Saranin, Nanotechnology 19 (2008) 245608.

[7] T. Hirahara, I. Matsuda, S. Yamazaki, N. Miyata, S. Hasegawa, T. Nagao, Appl. Phys. Lett. 91 (2007) 202106.

[8] T. Hirahara, T. Nagao, I. Matsuda, G. Bihlmayer, E.V. Chulkov, Yu.M. Koroteev, P.M. Echenique, M. Saito, S. Hasegawa, Phys. Rev. Lett. 97 (2006) 146803.

[9] T. Nagao, S. Yaginuma, M. Saito, T. Kogure, J.T. Sadowski, T. Ohno, S. Hasegawa, T. Sakurai, Surf. Sci. 590 (2005) L247.

[10] T. Kuzumaki, T. Shirasawa, S. Mizuno, N. Ueno, H. Tochihara, K. Sakamoto, Surf. Sci. 604 (2010) 1044.

[11] D.V. Gruznev, L.V. Bondarenko, A.Yu. Tupchaya, A.A. Yakovlev, E.A. Borisenko, M.V. Ryzhkova, D.A. Tsukanov, A.V. Zotov, A.A. Saranin „Na-induced Changes in Electronic Structure of Si(111)-β(√3×√3)-Bi Reconstruction“ (to be published).