

PHOTOEMISSION STUDY OF NANO SiC EPITAXIAL LAYERS SYNTHESIZED BY A NEW METHOD OF THE ATOM SUBSTITUTION IN Si CRYSTAL LATTICE

G.V. Benemanskaya^{1,2*}, P.A. Dementev^{1,2}, S.A. Kukushkin^{1,3}, M.N. Lapushkin^{1,2},
A.V. Osipov^{1,3}, B. Senkovskiy⁴, S.N. Timoshnev^{1,2}

¹Institute of Problems of Mechanical Engineering, Bolshoj pr. 61, V.O., St. Petersburg, 199178, Russia

²Ioffe Institute, Politekhnikeskaya 26, St. Petersburg, 194021, Russia

³ITMO University, Kronverksky Ave 49, St. Petersburg, 197101, Russia

⁴Helmholtz Zentrum Berlin für Materialien und Energie, Elektronenspeicherring BESSY II D 12489, Berlin,
Germany

*e-mail: Galina.Benemanskaya@mail.ioffe.ru

Abstract. Electronic structure of the SiC epitaxial nanolayer synthesized by a new method of the atom substitution in silicon crystal lattice has been first studied *in situ* in an ultrahigh vacuum using synchrotron radiation photoemission spectroscopy with photon energies in the range of 60–400 eV. Features of photoemission from the valence band and from both the Si 2*p*, C 1*s* core levels were revealed and shown to be provided by the high-quality clean SiC(111) sample with Si-rich surface. The photoemission from a surface state extending from the valence band maximum into gap was found. Three surface-related components of Si 2*p* core level were found. Only one surface component of the C 1*s* core level was found that indicates on one position of C atoms near the surface. The results support the full Si adlayer structure model of the SiC (111) surface that is characterized by Si- double layers, Si-dimers and Si adatoms.

1. Introduction

Production of high-quality wide-band gap semiconductor films of silicon carbide SiC, and others on silicon substrates is one of the substantial problem of micro- and opto-electronics. SiC is a very remarkable candidate for high power devices that can function under extreme conditions such as high temperature, high voltage, high power and frequency. Furthermore, SiC can be considered as promising material for biophysics applications owing to its low weight, high strength and extreme hardness [1-3]. Most of applications are oriented toward thin film geometries, where the surface and interface properties are of most important. All these applications require thorough studies of surface properties of SiC layers, and in particular, the interface formation. However, the surface electronic structure of SiC remains not clear and needs better understanding.

Solution of the problem will give the opportunity to integrate a number of new semiconductor materials in silicon electronics. The main obstacle to growing the low-defective SiC films on Si is the elastic stresses arising due to mismatch of the lattice parameters of semiconductor layer and silicon substrate. It forces engineers to develop very expensive methods to decrease elastic stresses using a variety of masks and buffer layers.

However, grown wide-gap semiconductor films contain many misfit dislocations yielding a significant degradation of the electro-physical properties of semiconductor materials. In this paper we present first photoemission studies of the SiC epitaxial nanolayer synthesized by a new method of the atom substitution in silicon crystal lattice

2. Conception of new method for growth of SiC epitaxial nanolayers

A new method was developed for the solid-phase synthesis of epitaxial layers when the substrate itself was involved into a chemical reaction and the reaction product grown in the interior of substrate layer [4, 5]. It was eliminated that the most advantageous location of the dipoles is the direction (111) in crystals with cubic symmetry. In the condition, the relaxation of the elastic energy is carried out due to attraction of point defects formed during the chemical reaction in anisotropic media.

The theoretically and experimentally implements of a completely new method of growing defect-free silicon carbide films on silicon substrate was proposed in the review [5] and references therein. The matter of this approach is based on the idea of preliminary incorporation of point defects into the crystal lattice of the silicon substrate. Such defects are both the C - carbon atoms placed in the Si interstitial positions and vacancies formed as a result of removal of one of the Si atoms. In the case of defects attracted to each other by the elastic interaction in the Si matrix, the resulting elastic energy caused by their incorporation into the substrate host is significantly lower than the energy of no interacting defects. It is well known that the spherically symmetric dilatation centers do not interact with each other at all in an isotropic medium of infinite size.

It was shown that dilatation centers can attract to each other in substantially anisotropic media, such as the crystal with the cubic lattice symmetry that provides the considerably decreasing the total elastic energy. These attractive centers form stable objects of a new type, namely, the elastic dilatation dipoles. The elastic energy of the system using heteroepitaxy of the SiC film on the cubic Si substrate is calculated as the example. It is shown that the elastic energy can relax completely only due to the ensemble of dilatation dipoles. It has been proven in [5] that the total elastic energy of a crystal during the formation of interacting defects inside its volume is

$$W(\cos \varphi(x, y, z)) = E_C + E_V + E_{int}(\cos \varphi(x, y, z)). \quad (1)$$

Here E_C and E_V are the elastic energies of the lattice distortion by the carbon atom and the vacancy. E_{int} denotes the energy of defects interaction.

$$E_{C,v} = \frac{2\mu^{Si} K^d (V^d - V^{Si,m})^2}{3K^d + 4\mu^{Si} 3V}, \quad (2)$$

where μ^{Si} is shear modulus of Si, K^d is the defect modulus of bulk compression, V^d is the defect volume occupied in silicon, V^{Si} is the volume per a single atom in silicon, V^m is the dimension of the interstitial position. For the interstitial solid solution, instead of the difference $V^d - V^{Si}$, it is necessary to use the quantity $V^d - V^m$, where V^m is the dimension of the interstitial position. V is a certain volume that in the framework of the theory of elasticity, can equally be written either as the defect volume or as the volume per atom of the basic matter:

$$E_{int}(\cos \varphi(x, y, z)) = -E_0(\cos^4 \varphi_x + \cos^4 \varphi_y + \cos^4 \varphi_z - 3/5), \quad (3)$$

where $\cos \varphi_i = x_i/r$ are the cosines between the axes x , y and z and a direction of the line connecting the centers of interacting defects:

$$E_0 = \frac{15K(3c_{11} - 4c_{44})\Omega^I \Omega^{II} \eta}{8\pi(c_{12} - 2c_{44})r^3} \quad (4)$$

where c_{11} , c_{12} , and c_{44} are the elasticity moduli of the cubic crystal, $r = x' - x$ is the position vector between the points x' and x and $\eta = (c_{11} - c_{12} - 2c_{44})/c_{44}$ is the crystal anisotropy parameter and $\Omega^{I,II}$ are the capacities of the first and second point defects. The expression $\cos^4 \varphi_x + \cos^4 \varphi_y + \cos^4 \varphi_z - 3/5$ reaches the minimum equal to -0.27 in the direction $\langle 111 \rangle$ that corresponds to an attraction of similar defects. The maximum of the expression equal to 0.4 is reached in the direction $\langle 100 \rangle$ corresponding to a repulsion of similar defects. Also it has a saddle point -0.1 in the direction $\langle 110 \rangle$. Therefore, the direction $\langle 111 \rangle$ represents the most energetically favorable for similar point defects. It corresponds to a situation when C atom is located along $(\bar{1}10)$ plane and under (111) planes in an interstitial position, whereas a vacancy is located along $\langle 111 \rangle$ direction with respect to it. In this case, the attraction between the silicon vacancy and the carbon atom (both of them are compressing dilation centers) reaches its maximum. The considered dilatation dipole provides the maximal relaxation of the elastic energy [5]. This mechanism of elastic energy relaxation is extreme efficient. Indeed, if dilatation centers do not attract to each other, the total elastic energy per SiC molecule is $W_{dil} = 0.22$ eV. But if one part of the dilatation dipole is the carbon atom, the elastic energy per SiC molecule is $W_{dip} = 0.13$ eV. Every 8 atoms of Si in the original matrix could be replaced by no more than 4 dilatation dipoles. Therefore, the relaxation maximum of the elastic energy due to dipoles corresponds to $\Delta W = (W_{dil} - W_{dip})/2 = 0.2$ eV per one molecule of SiC. It is shown, that the elastic energy can relax completely by dilatation dipoles because $W_{dil} - \Delta W \approx 0$.

The life time of dilatation dipoles at temperatures 1100–1250 °C is about $\sim 10^{-1} - 1$ s, that is three orders of magnitude larger than the formation time of the first SiC monolayer. So, the elastic dipoles play a role of ordering epitaxy centers. In the opposite case, the point defects repel being located along the $\langle 100 \rangle$ direction. In this situation, dipoles cannot arise and increase the elastic energy that leads to layers disorientation. In order to provide the effective application of a new relaxation mechanism of elastic energy due to the interaction between point defects, we propose the SiC deposition process not from the vapor phase but immediately from the matrix of the single crystalline Si substrate due to the chemical reaction between crystalline Si and gaseous carbon monoxide CO:



This reaction has been selected [5] because of the fact that the forming gaseous silicon monoxide SiO partially carries the atoms from the Si matrix inducing vacancies. Simultaneously, gaseous carbon monoxide CO is the source of carbon atoms C arranged in atomic voids of the silicon lattice. Both the Si vacancies and incorporated C atoms are the compressing dilatation centers in the cubic Si lattice and interact with each other. The chemical reaction (5) originates in two stages. At the first stage, the intermediate compound consisting of activating complex, namely, Si vacancy – C atom – Si matrix is formed. C atoms are placed in interstitial positions of Si matrix. At the second one the activating complex transforms into SiC, and released Si vacancies merge into pores in Si under the layer of SiC. It is revealed that the activating complex consists of the ensemble of dilatation dipoles ordered by the original Si matrix. The transition of the activating complex into both the SiC and pores is the structural phase transition of shifting type. In this phase transition the ordering of SiC molecules is followed by the original crystalline Si matrix. The mechanism of heterogeneous chemical reaction between gas and solid was investigated on using the

reaction (5). Conditions are found at which the dislocation-free growth of SiC films on Si substrates takes place. The new synthesis method proposed in [4] is fundamentally different from all currently existing methods of growing the SiC films on Si substrates.

Chemical components required for growing the SiC films on Si are supplied to the surface of the substrate when standard techniques are used. Therefore, the SiC films grow on the top surface of Si by the use of standard techniques. Using the new proposed method, the SiC layer is increased from inside the Si substrate that represents the different mechanism of SiC film growth. According to [5], this other mechanism allows us to grow not only 3C-SiC polytype, but some of its hexagonal polytypes.

Photoemission spectroscopy is an effective tool in observing electronic structure of both the semiconductor bulk and surface. Electronic structure of SiC(111) surface is insufficiently studied in contrast to the well investigated 6H-Si(0001) and Si(100) surfaces (see, for example [6-11]). Only a few works devote to investigate valence band and Si $2p$, C $1s$ core level spectra for SiC(111) [12-17]. Valence band structure of SiC(111) has been determined by XPS [15-17]. The photoemission studies of electronic structure of SiC(111) samples grown using new method have not been carried out yet. These issues are of great importance from fundamental and applied viewpoints. In this work, the first photoemission studies of the electronic structure of the SiC(111) epitaxial nanolayer obtained by a new method are presented.

2. Experiment

Photoemission studies were carried out at BESSY II, Helmholtz Zentrum, Berlin using the synchrotron radiation with photon energies in the range of 80–400 eV. Experiments were performed *in situ* in an ultrahigh vacuum of 5×10^{-10} Torr at room temperature. The spectra were collected in normal emission. For the new SiC nanolayer the photoemission spectra from the valence band (VB), spectra of surface states and Si $2p$, C $1s$ core-level spectra were recorded. A total energy resolution of better than 100 meV is used.

The single-crystal nano - SiC(111) epitaxial layer with the thickness of 70 nm has been grown on silicon (111) substrate owing to the chemical reaction with carbon monoxide. Grown high-quality single-crystal silicon carbide films do not contain misfit dislocations despite the huge lattice mismatch value. Also the possibility of growing of thick wide-gap semiconductor films on such templates SiC/Si(111) exists. Structure of SiC sample was ascertained by angle spectroscopic ellipsometric method and by roentgen microanalysis. Surface morphology of the sample was characterized by REED and atomic force microscopy AFM [4].

3. Results and discussion

Overview of the normal photoemission spectrum for the clean SiC(111) epitaxial layer at excitation energy of $h\nu = 450$ eV is presented in Fig. 1.

The spectrum clearly shows the main Si $2p$, Si $2s$ and C $1s$ core level peaks and denotes a lack of foreign contaminations. As can be seen, the photoemission from the valence band (VB) has small intensity and could be studied at lower excitation energies.

A number of first-principles calculations of the SiC(111) band structure and the density of states (DOS) have been performed [18-23]. Calculations based on the density functional theory within the local density approximation combined with an approach for correcting the band-gap have predicted such peculiarities. Moreover, these calculations showed that the surface structure below the Fermi level could be explained by Si-dangling bonds of SiC(111) surface [21-22]. However, more efforts should be made to explore and understand these results.

Figure 2 represents more detailed spectra of SiC in the valence band region at different excitation energies. A broad band of width ~ 10 eV is obtained.

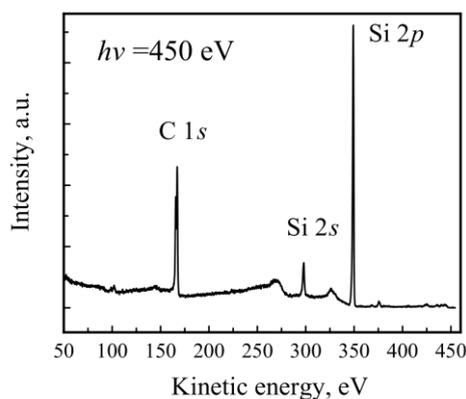


Fig. 1. Normal photoemission spectrum for the SiC(111). Excitation energy $h\nu = 450$ eV.

The energy position of the valence band maximum E_{VBM} at the surface is determined by extrapolating a linear fit to the leading edge of the valence band spectrum. For the clean SiC sample the spectra are characterized by the weakly structured band in the binding energy region of $0 \div 9$ eV below E_{VBM} with major peak at 3.8 - 4.0 eV and two feebly marked features at ~ 6 eV and at ~ 0.2 eV (see also Fig. 3).

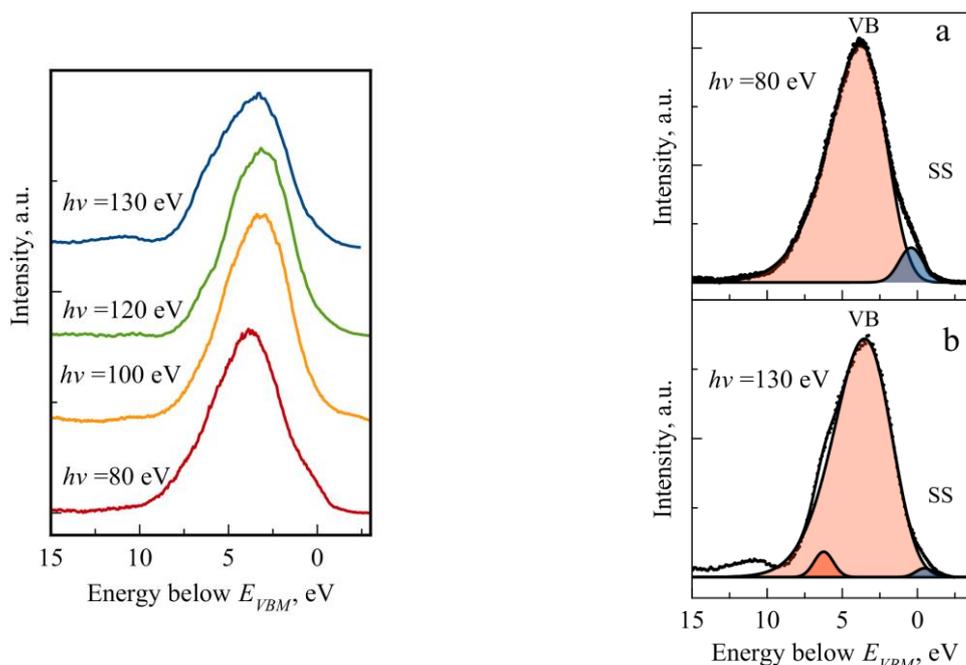


Fig. 2. The valence band photoemission spectra for the SiC(111) at different excitation energy.

Fig. 3. Decomposition of photoemission spectra for the SiC(111) at different excitation energy: (a) $h\nu = 80$ eV and (b) $h\nu = 130$ eV. Dots represent experimental data and solid lines represent fitting results with fitting components.

The similar UPS result was obtained for the single-crystal SiC(111) surface [15-17] and for the SiC(100) surface [9]. In addition to these photoemission studies the valence band spectrum with two clearly defined maxima is observed by XPS [11, 15]. The difference between UPS and XPS spectra can be related to the significant contribution in UPS results of both the surface and near surface region. The shape and the bandwidth of the valence band spectrum coincide well with results reported earlier [9, 10, 15, 25].

Result of a decomposition of normal photoemission spectra in the valence band region

for the SiC(111) epitaxial layer is represented in Fig. 3 a,b. We used two excitation energies (a) $h\nu = 80$ eV and (b) $h\nu = 130$ eV. The decomposition is carried out by separation of individual peaks according to the method published in [27] using Gaussian and asymmetric Gaussian functions. Data indicate the broad mayor maximum at energy of ~ 3 eV and additional peak with small intensity at energy of ~ 6 eV. Analysis of the spectrum coupled with DOS calculations [18] shows that both peaks can be associated with photoemission from the valence band. The analogical shape of the VB spectra was obtained for the SiC(111) [15] and for another surface reconstructions of SiC [9, 10].

Spectra show also the photoemission peak extending from energy region near E_{VBM} to gap. This peak labeled SS at binding energy of -0.5 eV is essentially increased in intensity as the excitation energy becomes less (Fig. 3a). A careful quantitative analysis shows that peak SS can be originated from a surface state. Under the assumption that shoulder SS is due mainly to intrinsic surface states, the results concur with theory [27] indicating a tail of Si $3p$ states extending from E_{VBM} to gap. Therefore, the peak SS can be originated from the Si surface dangling bonds.

Figure 4 shows photoemission spectra of the C $1s$ core level for the SiC(111) nanolayer and their line shape fits obtained at excitation energies of 330 eV and 450 eV. The C $1s$ core level spectrum is composed of two main components. The clear double structure is found indicating difference in the position of C atoms in the bulk and on the surface. The component labeled B at energy of 284.2 eV can be associated with bulk carbon atoms.

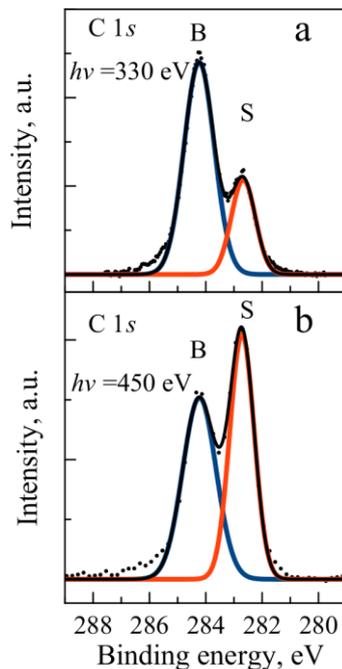


Fig. 4. Photoemission spectrum of the C $1s$ core level recorded from the SiC(111) at different excitation energies: (a) $h\nu = 330$ eV and (b) $h\nu = 450$ eV. Dots represent experimental data and solid lines represent fitting results with fitting components.

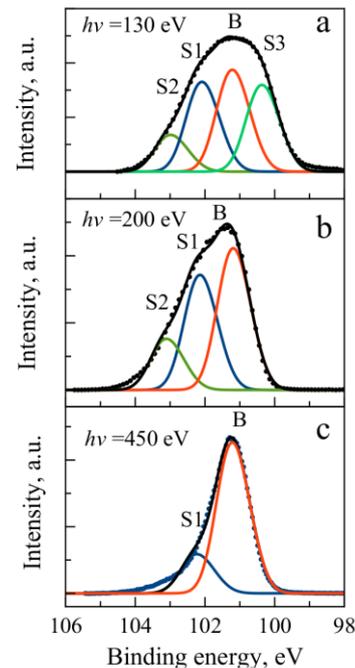


Fig. 5. Photoemission spectrum of the Si $2p$ core level recorded at different excitation energies: (a) $h\nu = 130$ eV, (b) $h\nu = 200$ eV and (c) $h\nu = 450$ eV. Dots represent experimental data and solid lines represent fitting results with fitting components.

An additional component S at about 282.5 eV can be associated with carbon atoms located near the surface region. The S component is shifted to the smaller binding energy by 1.6 ± 0.1 eV from the bulk B component which is an average value obtained from different SiC surfaces.

The intensity ratio of these components B/S is, however, rather arbitrary, since this

depends on the choice of the excitation energy. The increase in intensity ratio B/S at excitation energy of 450 eV can suggest the Si-rich surface with two Si surface layers [23]. If we take this result as evidence of a core-level shift in the third C layer, then the bonding between the second layer Si and third layer C is suggested to be less ionic than in the bulk. It is not reasonable to assign this S component as due to the graphite contamination since the C 1s binding energy of graphite was found to be ~ 2 eV larger than that of the carbon bulk component B [12-15, 17].

For the Si(111) surface three models of atomic reconstruction take place [23]. Until now, the correct type of atomic model is not known. It should be noted that the bulk structure of the SiC(111) is the same as that of Si except that Si double layers are replaced by Si-C bilayers, accompanied by a reduction of the lattice parameter. Therefore S- component of the C 1s core level can be corresponded to C-layer extended under Si – surface bilayer.

Figure 5 shows photoemission spectra of the Si 2p core level taken at different photon energies. The spectra could be fitted using a single spin-orbit split doublet and the spin-orbit splitting of the Si 2p 1/2 and Si 2p 3/2 components can be determined as ~ 0.6 eV. Three surface components are found for the Si 2p core level spectra. Previously two surface components were obtained for the Si(111) surface [13, 15].

Due to the difference in electron depth for the various excitation energy, we can predict that the energy of 450 eV corresponds to the bulk sensitivity excitation in contrast to the surface sensitivity excitation at 130 eV. Figure 5c shows the bulk component labeled B at energy of 100.8 eV and beside one surface shifted component S1 at energy of 102.2 eV. The peak labeled S1 is most easily seen in the surface sensitive spectra, and it is present in all the spectra by excitation from 130 eV to 450 eV (Fig. 5 a,b,c). The S2 component appears as a shoulder on the high binding energy side of the B peak (Fig. 5b). The spectrum exhibits the significant evolution at photon energy of 130 eV when three surface-related components S1, S2, S3 are revealed in the Si 2p spectrum (Fig. 5a). The presence of three surface-related components is evident to indicate that we deal with considerable reconstructed areas on the Si-rich surface. Considering the Si-rich nature of the SiC(111) one is inclined to assume strong similarities between the Si(111) 7x7 and SiC (111) 3x3 reconstructions. In fact, it has been proposed in [23] that the 3C-SiC(111) 3x3 reconstruction is energetically favorable, taken into account that by the Si enrichment the formation of both the Si-dimers and Si-adatoms configurations can take place. Three surface components S1, S2, S3 revealed for the Si 2p core level correspond well to the full Si adlayer structure model of the SiC (111) surface that is characterized by Si- double layers, Si-dimers and Si adatoms located on the surface.

4. Conclusion

Firstly, electronic structure of the nano-SiC epitaxial layer synthesized by a new method of the atom substitution in silicon crystal lattice has been first found using photoemission spectroscopy with photon energies in the range of 80 – 400 eV. Photoemission spectra in the VB region and both the Si 2p and C 1s core level spectra have been detailed studied for the SiC(111) epitaxial low-defect unstressed nano- layer. Secondly, the VB spectrum and both the Si 2p and C 1s core level spectra clearly identify the high-quality clean SiC(111) sample with Si-rich surface. The surface state near the valence band maximum with a small electron density is found to originate from Si surface dangling bands. Thirdly, three surface-related components of the Si 2p core level, namely S1, S2, and S3, are revealed in the spectra for the SiC(111) surface at lower excitation energy. On the contrary, the one surface-related component of the C 1s core level is observed at the major excitation energy. Results support the full Si adlayer structure model of the Si(111) surface with Si- double layer, Si-dimers and Si adatoms.

Acknowledgements

The authors of this work G.V. Benemanskaya, P.A. Dementev, S.A. Kukushkin,

M.N. Lapushkin, A.V. Osipov, S.N. Timoshnev were supported by grant # 14-12-01102 of Russian Science Foundation. The authors thank Synchrotron BESSY II and Russian-German Beamline, Synchrotron BESSY II, Helmholtz Zentrum, Berlin for providing the facilities to perform the experiments and for help during experiments.

References

- [1] S.E. Saddow, A. Agrawal, *Advances in Silicon Carbide Processing and Applications* (Artech Hous, 2004).
- [2] P. Souciassian, H.B. Enriquez // *Journal of Physics: Condensed Matter* **16** (2004) 1611.
- [3] T. Seyller // *Journal of Physics: Condensed Matter* **16** (2004) 1755.
- [4] S.A. Kukushkin, A.V. Osipov, S.K. Gordeev, S.B. Korchagina // *Technical Physics Letters* **31** (2005) 859.
- [5] S. A. Kukushkin, A.V. Osipov // *Journal of Physics D: Applied Physics* **47** (2014) 313001.
- [6] C. Persson, U. Lindefelt // *Journal of Applied Physics* **82** (1997) 5496.
- [7] L.I. Johansson, F. Owman, P. Martensson, C. Persson, U. Lindefelt // *Physical Review B* **53** (1996) 13803.
- [8] B. Wenzien, P. Kackell, F. Bechstedt, G. Cappellini // *Physical Review B* **52** (1995) 10897.
- [9] V.M. Bermudez, J.P. Long // *Applied Physics Letters* **66** (1995) 475.
- [10] H.W. Yeom, Y.-C. Chao, I. Matsuda, S. Hara, S. Yoshida, R.I.G. Uhrberg // *Physical Review B* **58** (1998) 10540.
- [11] L.I. Johansson, F. Owman, P. Martensson // *Physical Review B* **53** (1996) 13793.
- [12] Ryota Takahashi, Hiroyuki Handa, Shunsuke Abe, Kei Imaizumi, Hirokazu Fukidome, Akitaka Yoshigoe, Yuden Teraoka, Maki Suemitsu // *Japanese Journal of Applied Physics* **50** (2011) 070103.
- [13] M. Bosi, G. Attolini, M. Negri C. Frigeri, E. Buffagni, C. Ferrari, T. Rimoldi, L. Cristofolini, L. Aversa, R. Tatti, R. Verucchi // *Journal of Crystal Growth* **383** (2013) 84.
- [14] J. Su, Q. Niu, C. Tang, Y. Zhang, Zh. Fu // *Solid State Sciences* **14** (2012) 545.
- [15] P.-A. Glans, T. Balasubramanian, M. Syvajarvi, R. Yakimova, L.I. Johansson // *Surface Science* **470** (2001) 284.
- [16] R. Verucchi, L. Aversa, M.V. Nardi, S. Taioli, S. Beccara, D. Alfè, L. Nasi, F. Rossi, G. Salviati, S. Iannotta // *Journal of the American Chemical Society (JACS)* **134** (2012) 17400.
- [17] S.W. King, R.J. Nemanich, R.F. Davis // *Physica Status Solidi B* **252** (2015) 391.
- [18] C. H. Park, B.-H. Cheong, K.-H. Lee, K. J. Chang // *Physical Review B* **49** (1994) 4485.
- [19] P. Kackell, B. Wenzien, F. Bechstedt, P. Schiller // *Physical Review B* **50** (1994) 10761.
- [20] E.K.K. Abavare, J.-I. Iwata, A. Oshiyama // *Physical Review B* **87** (2013) 235321.
- [21] J. Furthmüller, F. Bechstedt, H. Hüsken, B. Schröter, W. Richter // *Physical Review B* **58** (1998) 13712.
- [22] J. Wang, L. Zhang, Q. Zeng, G.L. Vignoles, L. Cheng, A. Guette // *Physical Review B* **79** (2009) 125304.
- [23] J. Schardt, J. Bernhardt, U. Starke, K. Heinz // *Physical Review B* **62** (2000) 10335.
- [24] A. Ouerghi, M. Marangolo, R. Belkhou, S. El Moussaoui, M.G. Silly, M. Eddrief, L. Largeau, I.M. Portail, B. Fain, F. Sirotti // *Physical Review B* **82** (2010) 125445.
- [25] C. Virojanadara, M. Hetzel, L.I. Johansson, W.J. Choyke, U. Starke // *Surface Science* **602** (2008) 525.
- [26] L. Fleming, C.C. Fulton, G. Lucovsky, J.E. Rowe, M.D. Ulrich, J. Lüning // *Journal of Applied Physics* **102** (2007) 033707.
- [27] L. Wenchang, Y. Weidong, Z. Kaiming // *Journal of Physics: Condensed Matter* **3** (1991) 9079.