Ag and Pb diffusion on Ge(111)-3 × 2√3-Sn surface

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Ag and Pb diffusion on Ge(111)-3 × 2√3-Sn surface has been studied by Auger electron spectroscopy and low energy electron diffraction. The mechanism of diffusion of atoms of these elements along the Ge(111)-3 × 2√3-Sn surface is determined, and the temperature dependences of the diffusion coefficients are measured. The diffusion parameters of Ag along the Ge(111)-3 × 2√3-Sn and Si(111)-2√3 × 2√3-Sn surfaces are compared.

Keywords: surface, surface diffusion, Ge(111), Ag, Pb, Sn.

1. Introduction

Metals on the surface of semiconductors are of considerable interest, both from a scientific and practical point of view. Structures formed on the surface with the amount of deposited metal from a fraction of a monolayer to several monolayers have a variety of structural and electronic properties. The most widely conducted studies of single-component structures of metals such as Ag, Pb, Sn, Au, In, Tl on silicon and germanium [1–6]. Using the second element can lead to two-component structures (Ag, Au) [7], (In, Au) [8], (In, Pb) [9,10], (Sn, Ag) [11,12]. The second element, in some cases, can be used as a surfactant. Surfactants change the energy of the surface and thereby affect the processes (mobility, embedding in the edges of steps, etc.) that occur on it during the growth of adsorbed metals. Thus, for the formation of well-ordered Ag films on Si(111), its deposition is carried out at a temperature of 100 K, and the formation of atomic-flat films with a thickness of less than 5 ML (ML — monolayer) is difficult [13,14]. Adsorption of Ag on a Si(111) surface with a preformed structure $\sqrt{3} \times \sqrt{3}$-Ga or $\sqrt{3} \times \sqrt{3}$-In or $\sqrt{3} \times \sqrt{3}$-Sn leads to the formation of ordered Ag films at room temperature, and their thickness may be less than 5 ML [15–17].

Diffusion of Sn, Ag and Pb both over the atomically clean Si(111) surface and the atomically clean Ge(111) surface occurs by the solid-phase spreading mechanism [18–21]. In this case, the diffusion coefficients of metal atoms on clean surfaces are much smaller than for the surface phases formed by these atoms. At the same time, the atoms that make up the surface phase are stationary. Surface phases are formed on the surface $2\sqrt{3} \times 2\sqrt{3}$-Sn, $\sqrt{3} \times \sqrt{3}$-Ag, HIC-Pb (Hexagonal InCommensurate structure consisting of domains of the structure $\sqrt{3} \times \sqrt{3}$-Pb, separated by domain walls [22]) and $3 \times 2\sqrt{3}$-Sn, $\sqrt{3} \times \sqrt{3}$-Ag, $\sqrt{3} \times \sqrt{3}$-Pb, respectively. Earlier we found that the diffusion coefficients of Ge over the surface of Si(111)-$2\sqrt{3} \times 2\sqrt{3}$-Sn is several orders

of magnitude larger than on a clean surface [23]. The mobility of Ag atoms on this surface is also much greater than on a clean surface, and the diffusion coefficient depends on the concentration of atoms [24]. Surface phases Si(111)-$2\sqrt{3} \times 2\sqrt{3}$-Sn and Ge(111)-$3 \times 2\sqrt{3}$-Sn have similar properties, so at a temperature of $\sim 200°$C they reversibly rearrange to form surface phases 1×1-Sn [25]. The values of the tin diffusion coefficients for these phases are very close [18,21]. It is possible that the mobility of silver and lead atoms over the tin-induced surface phase of Ge(111)-$3 \times 2\sqrt{3}$-Sn will also be higher than on a clean surface Ge(111).

The purpose of this work was to establish the mechanisms of diffusion of mass transfer of Ag and Pb atoms over the surface phase $3 \times 2\sqrt{3}$-Sn formed on the atomically clean surface of Ge(111), to construct temperature dependences of diffusion coefficients and to compare the diffusion parameters of Ag on Ge(111) surfaces and Si(111).

2. Experimental procedure

The experiments were carried out in a LAS-2000 (Rib) setup on germanium (111) *p*-type samples with a resistance of about $5\,\Omega \cdot$ cm and dimensions of $22 \times 5 \times 0.3$ mm. To obtain an atomically clean surface with a structure C(2×8) (Fig. 1,*a*), its purification was carried out by means of several cycles of etching the surface with Ar ions with an energy of 750 eV and annealing of samples at a temperature of 700°C. The samples were heated by passing an alternating current. The temperature of the samples was measured using an infrared pyrometer. In the temperature range $200-350°$C, the temperature was determined using a thermocouple. The surface structure was controlled by the low energy electron diffraction (LEED), and the surface composition — using the Auger electron spectroscopy (AES). The peaks Ag (351 eV), Sn (430 eV), Pb (94 eV) and Ge (1147 eV) were used. The diameter of the primary electron beam in the Auger spectrometer was about $15\,\mu$m,
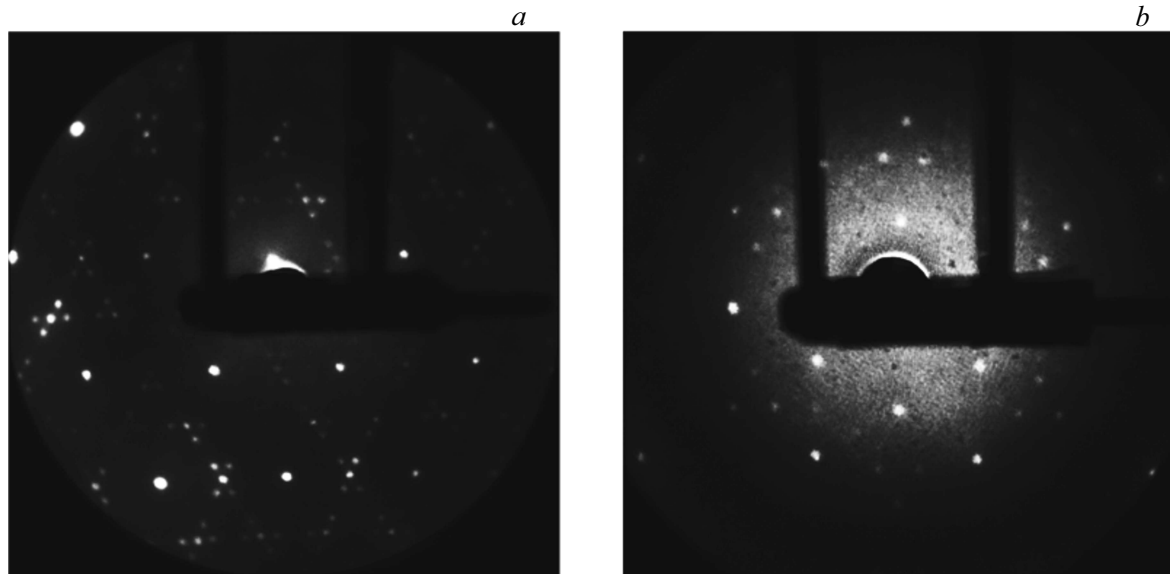
Figure 1. Diffraction patterns *a* — atomically clean Ge(111)-C(2 × 8) surface (90 eV), *b* — Ge(111)-3 × 2$\sqrt{3}$-Sn surfaces (70 eV).

the energy of the primary electrons was 3 keV. The diameter of the primary beam in the SED system had a value of the order of 0.8 mm. The EAS sensitivity was at least 2 at.% by Ge, 0.1 at.% by Ag, 0.2 at.% by Sn and 0.3 at.% by Pb.

Concentrations were calculated based on the model of homogeneous distribution of elements using the coefficients of elemental sensitivity taken from the work [26]. When calculating the Ag concentration using the peak Ag (351 eV), the close location of the peak Sn (367 eV) was taken into account. To do this, on the surface with the formed structure 3 × 2$\sqrt{3}$-Sn, a peak Sn (430 eV) and an Auger signal were recorded in the energy range in which the peak Ag (351 eV) was recorded. The intensity of the received signal was taken into account when calculating the concentration of Ag at each distribution point $C_{Ag}(x)$ proportional to the intensity of the peak Sn (430 eV) at the same point.

Formation of the Ge(111) surface phase-3 × 2$\sqrt{3}$-Sn was carried out by depositing 1.1−1.2 ML (for Ge(111) 1 MS is 7.21 · 10^{14} at/cm^2) tin [27] on an atomically clean sample surface heated to 400°C. The diffraction pattern from such a surface is shown in Fig. 1, *b*. The deposition rate of Sn was about 0.05 ML/min at a pressure of 2−4 · 10^{-8} Pa.

The source of Ag and Pb atoms in the diffusion study was a strip of silver or lead with a sharp boundary deposited on the surface of a germanium sample with the structure 3 × 2$\sqrt{3}$-Sn. The thickness of the strips was ∼ 10 ML with a sharp border. The width of the strip was ∼ 4 mm. The edge of the strip was perpendicular to the long side of the sample. The strip was formed using a collimator. The blurring of the edge of the strip associated with the geometry of the location of the source, collimator and sample was no more than 20 μm. The deposition rate of Sn was about 0.1 ML/min at a pressure of 2−4 · 10^{-8} Pa. The concentration of impurities in Sn, Ag and Pb did not exceed 10^{-2} at.%.

3. Results

3.1. Diffusion of silver over surface Ge(111)-3 × 2$\sqrt{3}$-Sn

On the surface of Ge(111)-3 × 2$\sqrt{3}$-Sn after annealing in the temperature range 300−400°C, concentration distributions of $C_{Ag}(x, t)$ were observed, where x is the distance from the source of silver atoms, and t is the annealing time. A typical concentration distribution is shown in Fig. 2. The shape of the distributions is characteristic of diffusion proceeding by the random walk mechanism. The resulting distributions are described by the expression

$$C(x, t) = C_0 erfc\left(\frac{x}{2\sqrt{Dt}}\right), \tag{1}$$

where C_0 — the concentration of atoms at $x = 0$. In Fig. 2, a solid line shows the theoretical distribution obtained for the diffusion coefficient calculated from the experimental distribution points $C_{Ag}(x)$ using the expression (1). The temperature dependence of the diffusion coefficients obtained using the equation (1) is shown in Fig. 3 and is described by the expression $D_{Ag/Ge(111)-3×2\sqrt{3}-Sn} = 0.1\exp(-0.6 \text{ eV}/kT) \text{ cm}^2/\text{s}$. Figure 3 also shows the temperature dependence of the diffusion coefficients of silver on the Ge(111) surface-$\sqrt{3} × \sqrt{3}$-Ag [20] described by the expression $D_{Ag/Ge(111)-\sqrt{3}×\sqrt{3}-Ag} = 2.2\exp(-0.9 \text{ eV}/kT) \text{ cm}^2/\text{s}$.

Extrapolating the dependence $D_{Ag/Ge(111)-\sqrt{3}×\sqrt{3}-Ag}(T)$ to 300°C, we obtain that in the temperature range 300−400°C, the values of the diffusion coefficients of silver over a surface with a structure of 3 × 2$\sqrt{3}$-Sn exceed the corresponding values on $\sqrt{3} × \sqrt{3}$-Ag surface by more than an order of magnitude.

Diffusion of silver both on the surface of Si(111)-2$\sqrt{3}$ × 2$\sqrt{3}$-Sn [24], and Ge(111)-3 × 2$\sqrt{3}$-Sn

occurs by the random walk mechanism, but on the surface Si(111)-$2\sqrt{3} \times 2\sqrt{3}$-Sn there is a dependence of the diffusion coefficient on the concentration of diffusing atoms, and on Ge(111)-$3 \times 2\sqrt{3}$-Sn this dependency could not be established. Surface phases Si(111)$2\sqrt{3} \times 2\sqrt{3}$-Sn and Ge(111)-$3 \times 2\sqrt{3}$-Sn at a temperature of $\sim 200°$C reversibly rearrange to form surface phases 1×1-Sn [25]. That is, the diffusion of silver atoms on the surfaces of silicon and germanium at temperatures above 200°C occurs in the surface phases of 1×1-Sn. Cooling of the samples
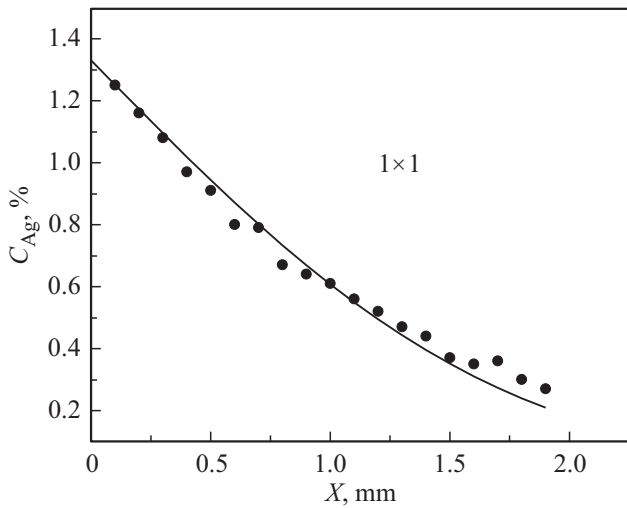
Figure 2. Experimental concentration distribution $C_{Ag}(x)$(points) on the Ge(111)-$3 \times 2\sqrt{3}$-Sn surface after annealing at 300°C for 250 min and the theoretical distribution (solid line) obtained using the calculated diffusion coefficient. The boundary of the deposited Ag strip, which serves as a source of diffusing atoms, is at $x = 0$ mm.
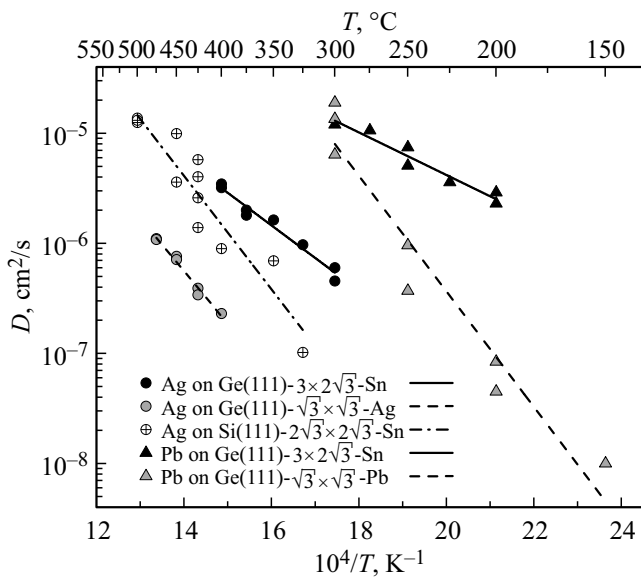
Figure 3. Dependences of Ag diffusion coefficients on Ge(111)-$3 \times 2\sqrt{3}$-Sn, Ge(111)-$\sqrt{3} \times \sqrt{3}$-Ag [21], Si(111)-$2\sqrt{3} \times 2\sqrt{3}$-Sn [24] surfaces for Ag concentration 0.85 at.% and Pb on Ge(111)-$3 \times 2\sqrt{3}$-Sn and Ge(111)-$\sqrt{3} \times \sqrt{3}$-Pb [21] from temperature.
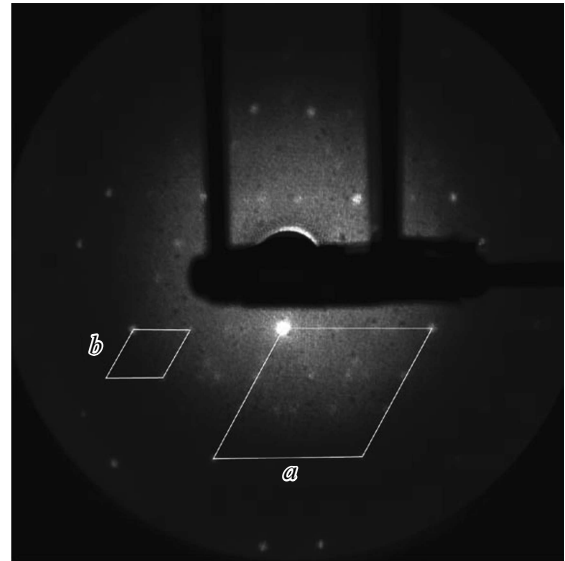
Figure 4. Diffraction pattern (72 eV) from an incommensurable surface structure that is observed on the surface of Ge(111)-$3 \times 2\sqrt{3}$-Sn with a silver strip sprayed on it. The elementary cells 1×1 of the unreconstructed Ge(111) surface and the incommensurable structures are denoted as *a* and *b*, respectively.

leads to the fact that the surface phase $2\sqrt{3} \times 2\sqrt{3}$-Sn is restored on the surface Si(111) occupied by the distribution $C_{Ag}(x,t)$ [24], whereas on Ge(111) the surface phase 1×1 remains up to the concentration of silver ~ 0.1 at.%. At lower concentrations, the surface phase $3 \times 2\sqrt{3}$-Sn is observed. The value of the diffusion coefficient of silver on the surface Si(111)-$2\sqrt{3} \times 2\sqrt{3}$-Sn depends on its concentration. It grows with a decrease in the concentration of silver. At the same time, the value of the diffusion activation energy decreases. Figure 3 shows the temperature dependence of the diffusion coefficients of silver on the surface of Si(111)-$2\sqrt{3} \times 2\sqrt{3}$-Sn for a minimum silver concentration of 0.85 at.% of the obtained in the work [24] This dependence is described by the expression $D_{0.85\,Ag/Si(111)-2\sqrt{3}\times2\sqrt{3}\text{-Sn}} = 68\exp(-1.0\,\text{eV}/kT)\,\text{cm}^2/\text{s}$. The values of the diffusion coefficients of silver on this surface are closer to the corresponding values on the surface of Ge(111)-$3 \times 2\sqrt{3}$-Sn than on the surface of Ge(111)-$\sqrt{3} \times \sqrt{3}$-Ag.

A diffraction pattern was observed on the surface occupied by a strip serving as a source of silver atoms, as shown in Fig. 4. This picture corresponds to a surface structure incommensurable with the unit cell of an unstructured Ge(111) surface. The vectors of an elementary cell of incommensurable structure are approximately 2.7 times larger than the corresponding vectors of the surface Ge(111).

3.2. Diffusion of lead over surface Ge(111)-3 × 2√3-Sn

Concentration distributions $C_{Pb}(x,t)$ on the Ge(111)-$3 \times 2\sqrt{3}$-Sn surface were obtained in

the temperature range $200-300°C$. The shape of the distributions is similar to that shown in Fig. 2 and corresponds to diffusion by the random walk mechanism. The diffusion coefficients were calculated using the expression (1). The temperature dependence of the diffusion coefficients is shown in Fig. 3 and is described by the expression $D_{Pb/Ge(111)\text{-}3x2\sqrt{3}\text{-Sn}} = 4.5 \exp(-0.4\,\text{eV}/kT)\,\text{cm}^2/\text{sec}$. The dependence of the diffusion coefficients of lead on its concentration, as well as silver, on the surface of Ge(111)-$3 \times 2\sqrt{3}$-Sn could not be detected. The diffusion of lead, like silver, leads to the fact that on the surface where the concentration of lead exceeds the value of ~ 0.5 at.%, after cooling the sample to room temperature, the structure of 1×1 is observed. At lower concentrations, the original structure of $3 \times 2\sqrt{3}$ is restored. The structure of $\sqrt{3} \times \sqrt{3}$ was observed on the surface occupied by a strip of lead. Figure 3 also shows the temperature dependence of the diffusion coefficients of lead over the Ge(111)-$\sqrt{3} \times \sqrt{3}$-Pb surface [21] described by the expression $D_{Pb/Ge(111)\text{-}\sqrt{3}\times\sqrt{3}\text{-Pb}} = = 5.3 \cdot 10^3 \exp(-1.0\,\text{eV}/kT)\,\text{cm}^2/\text{sec}$. In the temperature range $200-300°C$, the values of the diffusion coefficients of lead over a surface with a structure of $3 \times 2\sqrt{3}$-Sn are greater than the corresponding values on the surface of $\sqrt{3} \times \sqrt{3}$-Pb, but the differences are less than in the case of silver diffusion.

4. Conclusion

The mechanisms of diffusion of silver and lead atoms over a surface with a Ge(111)-$3 \times 2\sqrt{3}$-Sn structure have been established. The diffusion of silver and lead atoms over this surface proceeds by a random walk mechanism. The temperature dependences of the diffusion coefficients of the atoms of these elements are obtained. The dependence of the diffusion coefficients of silver and lead atoms on their concentration, in contrast to the diffusion of silver atoms over the surface of Si(111)-$2\sqrt{3} \times 2\sqrt{3}$-Sn [22], is not observed.

It is found that the values of the diffusion coefficients of silver and lead atoms over the surface of Ge(111)-$3 \times 2\sqrt{3}$-Sn in the considered temperature ranges is greater than the corresponding values for Ge(111)-$\sqrt{3} \times \sqrt{3}$-Ag and Ge(111)-$\sqrt{3} \times \sqrt{3}$-Pb, and the activation energy is less. The values of the diffusion coefficients of silver atoms on the surfaces of Ge(111)-$3 \times 2\sqrt{3}$-Sn and Si(111)-$2\sqrt{3} \times 2\sqrt{3}$-Sn for a silver concentration of 0.85 at.% are close.

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Conflict of interest

The author declares that he has no conflict of interest.

References

[1] H.M. Sohail, R.I.G. Uhrberg. Surf. Sci. **635**, 55 (2015).

[2] X.-Y. Ren, H.-J. Kim, S. Yi, Yu Jia, J.-H. Cho. Phys. Rev. B **94**, 075436 (2016).

[3] R. Cortés, A. Tejeda, J. Lobo, C. Didiot, B. Kierren, D. Malterre, E.G. Michel, A. Mascaraque. Phys. Rev. Lett. **96**, 126103 (2006).

[4] W.H. Choi, P.G. Kang, K.D. Ryang, H.W. Yeom. Phys. Rev. Lett. **100**, 126801 (2008).

[5] Eli Rotenberg, H. Koh, K. Rossnagel, H. W. Yeom, J. Schäfer, B. Krenzer, M.P. Rocha, S.D. Kevan. Phys. Rev. Lett. **91**, 246404 (2003).

[6] P. Garcia-Goiricelaya, I.G. Gurtubay, A. Eiguren. Phys. Rev. B **97**, 201405 (2018).

[7] X. Tong, C.S. Jiang, S. Hasegawa. Phys. Rev. B **57**, 9015 (1998).

[8] J.K. Kim, K.S. Kim, J.L. Mc Chesney, E. Rotenberg, H.N. Hwang, C.C. Hwang, H.W. Yeom. Phys. Rev. B **80**, 075312 (2009).

[9] H.M. Sohail, R.I.G. Uhrberg. Surf. Sci. **649**, 146 (2016).

[10] S. Owczarek, L. Markowski. Surf. Sci. **693**, 121552 (2020).

[11] H.M. Sohail, J.R. Osiecki, R.I.G. Uhrberg. Phys. Rev. B **85**, 205409 (2012).

[12] H.M. Sohail, R.I.G. Uhrberg. Surf. Sci. **644**, 29 (2016).

[13] L. Huang, S.J. Chey, J.H. Weaver. Surf. Sci. **416**, L1101 (1998).

[14] H. Hirayama. Surf. Sci. **603**, 1492 (2009).

[15] S. Starfelt, H.M. Zhang, L.S.O. Johansson. Phys. Rev. B **97**, 195430 (2018).

[16] S. Starfelt, L.S.O. Johansson, H.M. Zhang. Surf. Sci. **692**, 121531 (2020).

[17] S. Starfelt, R. Lavén, L.S.O. Johansson, H.M. Zhang. Surf. Sci. **701**, 121697 (2020).

[18] A.E. Dolbak, B.Z. Olshanetsky. FTT, **52**, 1215 (2010).(in Russian).

[19] A.E. Dolbak, B.Z. Olshanetsky. ZhETF **143**, 1105 (2013). (in Russian).

[20] A.E. Dolbak, R.A. Zhachuk, B.Z. Olshanetsky. Central Eur. J. Phys. **2**, 254 (2004).

[21] A.E. Dolbak, B.Z. Zhachuk. ZhETF **156**, 467 (2019). (in Russian).

[22] S. Stepanovsky, M. Yakes, V. Yeh , M. Hupalo, M.C. Tringides. Surf. Sci. **600**, 1417 (2006).

[23] A.E. Dolbak, B.Z. Olshanetsky. Central Eur. J. Phys. **6**, 634 (2008).

[24] A.E. Dolbak, B.Z. Olshanetsky. ZHETF **147**, 313 (2015). (in Russian).

[25] Toshihiro Ichikawa. Surf. Sci. **140**, 37 (1984).

[26] P.W. Palmberg, G.E. Riach, R.E. Weber, L.E. Davis, N.C. Mac Donald. Handbook of Auger Electron Spectroscopy. Phys. Elek. Ind. Inc., Minnesota (1976).

[27] T. Ichikawa. Surf. Sci. **140**, 37 (1984).