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EFFECT OF Ge(111) SURFACE TREATMENT ON LOW-ENERGY ELECTRON BACKSCATTERING

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Using low-energy electron backscattering technique with a high-resolution electron spectrometer, the effect of Ge(111) surface treatment on low-energy electron backscattering in the energy range 0.5–3.0 eV is studied. A possibility of control of electron properties of Ge(111) by surface treatment is shown. Features, observed in energy loss spectra, are related to the excitation of electron transitions between the density-of-states maxima in the valence band and conduction band of the reduced Brillouin zone and surface electron states for the surfaces under investigation.

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1. Introduction

The most widely used emission techniques of studies of filled electronic states of solids are ultraviolet and X-ray photoelectron spectroscopy with angular resolution. Information about unfilled electronic states can be obtained from electron-photon spectroscopy and low-energy electron diffraction [1–6]. A characterisctic feature of these experiments is that the energy of exciting particles does not exceed 10 eV. The elaborated technique of low-energy electron backscattering (LEEB) the primary electron beam energy (E_p) varies practically from 0 eV to 10 eV. This enables both bulk and surface electron states to be probed since in this energy range average free path of electrons in a solid with respect to inelastic collisions varies logarithmically from ~10^3 Å for 1 eV to ~10 Å for 10 eV [1,3,4,7]. Besides, at E_p<10 eV the interaction is localized in a thin near-surface area, hence due to Heisenberg uncertainty relation a considerable uncertainty of normal constituent of the electron momentum p occurs and quantum-mechanical selection rules relax [1,2]. While in the case of photoemission one can neglect the photon pulse with respect to the emitted electron pulse, at slow electron scattering their pulse should be taken into account since at the energy ~10 eV the electron wavevector k~1.6×10^{10} m^{-1} is of the same order as Brillouin zone dimensions in the k-space. Therefore, at the excitation by electrons with the energy E_p ~0–10 eV both direct and indirect allowed and forbidden transitions of electrons from filled to unfilled bands over the entire reduced Brillouin zone, including surface electron states (SES), are possible.

Our earlier studies of mirror-polished Ge(111), Ge(110), Ge(100) faces have shown that the reconstruction of their surfaces occurs in similar blocks. For these objects new surface electron states in the gap with energies ~0.18 eV and ~0.25 eV were revealed [8–10]. Studies of coefficient of slow electron elastic reflection from mechanically polished, etched and ground Ge(111) surface have shown it to be maximal for the mirror surface etched by a polishing solution, and minimal for the ground surface [11].

The present paper is aimed at the studies of effect of Ge(111) surface treatment on the processes of inelastic electron backscattering in the energy range 0.5–3.0 eV.

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2. Experimental setup and objects of investigation

The measurements of the energy loss spectra were carried out *in situ* in ultrahigh vacuum at residual gas pressure in the vacuum chamber (1–2)$\times 10^{-7}$ Pa. The main unit of the setup is an original hypocycloidal electron spectrometer (HES). HES enables the investigation of energy dependences of elastically backscattered slow electron beam intensity as well as energy loss spectra in the energy range 0–10 eV when the electron beam is incident and reflected normally to the surface within a small solid angle (~1–2°) centered in the beam incidence point. Such scattering geometry could be realized due to the fact that in crossed electric and magnetic fields required for the spectrometer operation electrons, besides the directed motion, drift in a transverse direction. This drift value does not depend on the electron vecocity vector. Therefore, the backscattered electrons having passed the analyser crossed beams shift by some distance with respect to the primary beam axis. By placing a collector in this point one can detect electrons, scattered back (by ~180°). This geometry of the experiment is very effective for investigation of resonances of surface states since in this case the contribution of the resonance scattering is essentially higher in comparison with other scattering processes [1]. The detailed description of the setup, the hypocycloidal spectrometer and the measurement technique is given in [12–14]. In this experiment the characteristics of the spectrometer were the following: primary electron beam current ~10^{-8}A, the beam diameter ~0.5 mm, full width at half maximum of the energy distibution of electrons in the primary beam (FWHM) ~ 30–40 meV, analyser energy resolution (FWHM) ~ 50 meV, transmission ~98%. The measurement process is automated. The signal in each point was integrated over 5–10 s, averaged and recorded in a database. The analysis of the experimental data was performed using a multiple set of measurements. The accuracy of determination of energy position of the peak of the features in the spectra was ±50 meV, the intensity uncertainty not exceeding 3–5%.

We have studied the LEEB energy loss spectra at different incident electron energies within the range E_p=0.5–3.0 eV for differently modified Ge(111) surfaces. The energy loss was scanned with a step of 5–10 meV. The scale was calibrated by the energy position peak of the elastically backscattered electrons. The calibration accuracy was ±40–50 meV. The reliability of the obtained results was provided by precise devices and high reproducibility of the results in a multiple set of measurements.

The investigated (111) surfaces of an extra pure germanium single crystal were oriented by characteristic reflexes using Cu K_α X-ray radiation within the accuracy of 1°. Three types of Ge(111) surfaces were studied. The surface of the first sample was ground, the second one was mirror-polished mechanically, the third one was mirror-polished mechanically and subsequently etched by a polishing solution of $5HNO_3+3HF+3CH_3COOH$ during 120 sec according to the procedure described in [15].

For all Ge(111) surfaces under investigation X-ray diffractometric studies of the shape of maxima of coherent scattering intensity, typical for this plane, were performed. The Ge(111) single crystal surface roughness parameter R_α was ~ 0.20 μm for the ground surface, ~0.007 μm for the polished surface, and ~0.005 μm for the etched surface. Note that all the surfaces under study were optically uniform.

Prior to the experiments the spectrometer and the samples were treated by ultrasound in ethanol. Further refinement of all the surfaces under investigation was performed by heating of the samples to 1000–1100 K in the vacuum 10^{-7} Pa during 5h under bombardment from the rear side by high-energy electrons (U~500 V, I~35 mA). In order to provide the surface cleanness several heating/cooling cycles were performed. The cleanness was checked by the presence of distinct and constant fine structure in the backscattering spectra, characteristic for the given surface.

3. Results and discussion

It is known that at heating of atomically pure (111) surface of germanium above 450 K an irreversible (2×8) superstructure is formed for which the Fermi level (E_F) practically coincides with the valence band maximum [2]. The analysis of the reference data shows that the SES spectrum of the atomically pure Ge(111)-2×8 surface is characterized by the presence of three groups of levels (See Fig. 1). The first group of SES is located below the valence band maximum and consists of two surface bands with the width of 0.2 eV with the density-of-states maxima at –1.4 eV and –0.85 eV [16–19] as well as local SES with the energies –1.1 eV [17–19] and –0.4 eV [2,17,20]. The SES of the second group are located on both sides of the Fermi level: a donor band below E_F by 0.02 eV and an acceptor band above E_F by 0.02 eV [2,21]. These states determine the value and sign of the surface charge as well as the near-surface band bending [2]. The third group includes SES located in the gap with the density-of-states maxima at 0.18 eV, 0.27 eV [9,10], 0.4 eV and 0.45 eV [2,22,23].

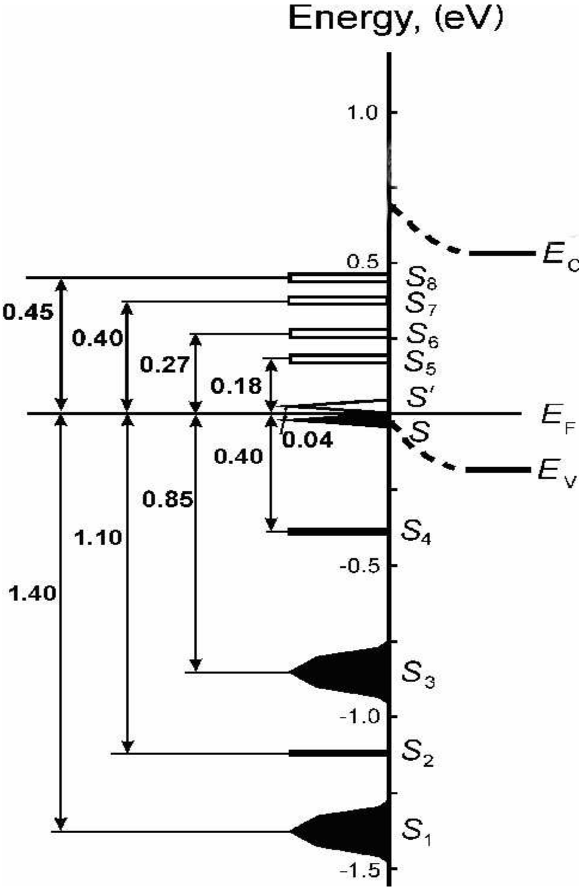


Fig. 1. The spectrum of surface electron states for Ge(111)-2×8.

As we have shown earlier for the studies of mechanically mirror-polished Ge(111), Ge(110) and Ge(100) surfaces, the shape of the energy loss spectra depends on the incident electron energy in the range 0.4–3.0 eV [8–10]. This is also confirmed by the data presented here for the ground, polished and etched surfaces of Ge(111). Fig. 2 shows the loss spectra at different energies E_p=0.5–3.0 eV for the Ge(111) surface etched by the polishing solution. As seen from the figure, the energy loss spectra reveal a distinct fine structure, both the shape of the spectra and the features being essentially dependent of E_p.

Energy loss spectra at different energies E_p for differently modified Ge(111) surfaces are shown in Fig. 3. The energy positions of the maxima in the spectra, averaged over multiple sets of measurements for differently treated Ge(111) surfaces at E_p=0.5–3.0 eV are given in Table 1. Besides, the same table contains the possible electron transitions responsible for the maxima with the account of the SES spectra for Ge(111)-2×8 (Fig. 1) and the energy structure of germanium calculated by *GW* approximation and orthogonalized plane-wave method [24–26]. The analysis of the experimental data shows the energy positions of the features in the loss spectra to be close for the three surfaces under investigation with the account of the experimental error (±50 meV). However, as seen from Fig. 3, the shape of the energy loss spectra for each surface essentially depends on the incident electron energy.

The low-energy features in the LEEB loss spectra below 0.60 eV are revealed for all surfaces only for E_p < 1.0 eV (Fig. 3 a, b), and the features above 0.60 eV are seen in all spectra at E_p >1.0 eV (Fig. 3 c-h).

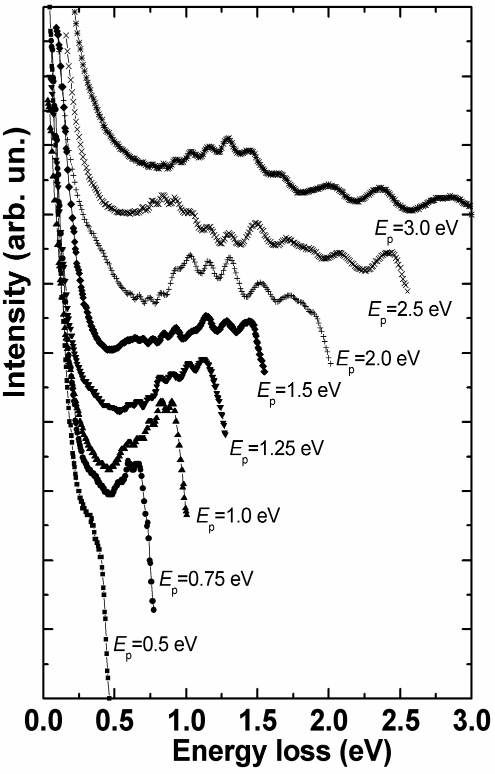
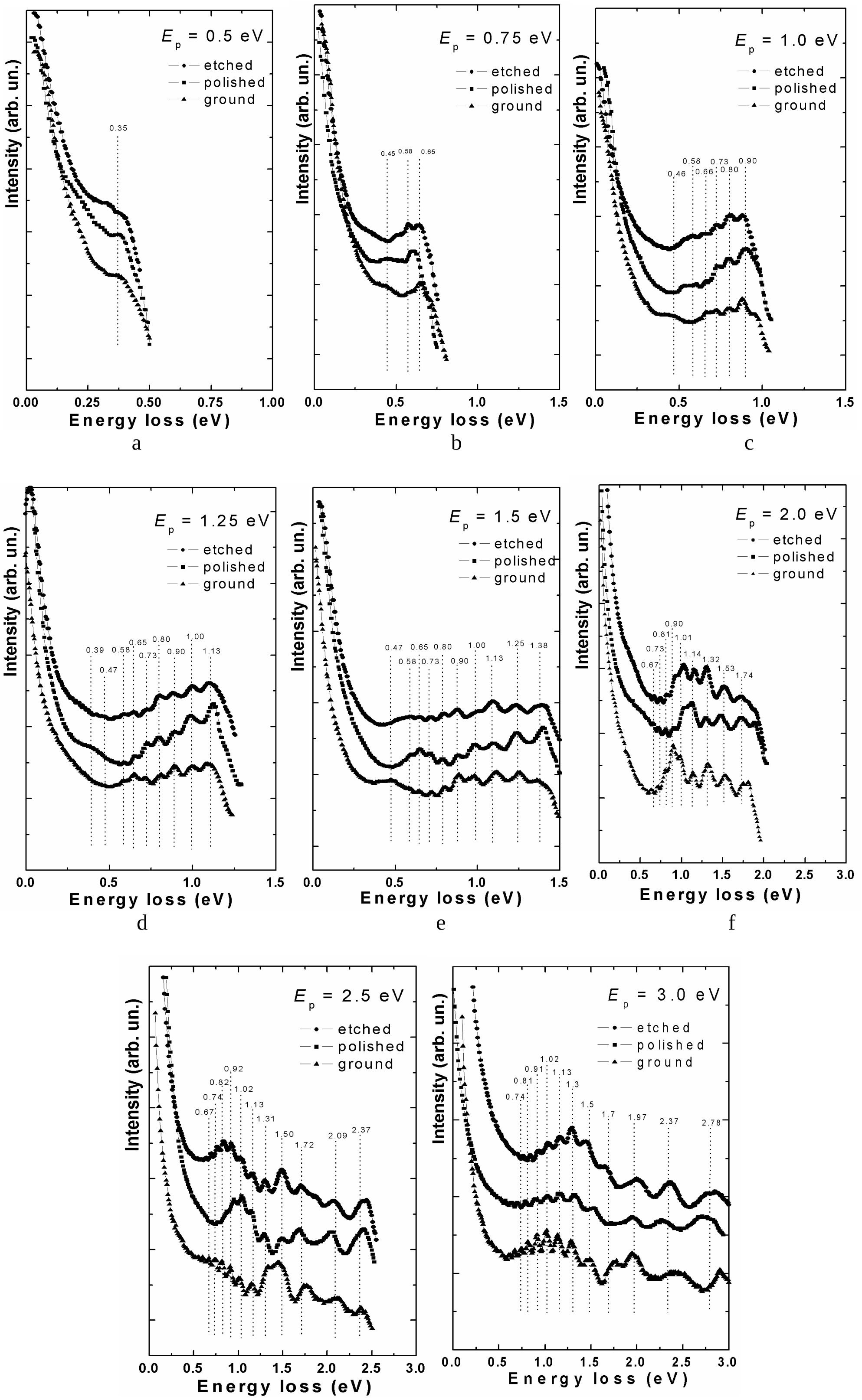


Fig. 2. LEEB energy loss spectra for the etched Ge(111) surface at different incident electron energies E_p

At E_p=0.75 eV (Fig. 3b) the loss spectra in the energy range 0.40–0.70 eV contain the features at ~0.45 eV, ~0.58 eV and ~0.65 eV. The feature at ~0.45 eV which can result from electron transitions from the bulk valence band maximum Γ'_{25} (0 eV) and/or from the filled SES *S* to the empty SES S_8 above the Fermi level, is revealed as a relatively broad maximum for the ground and polished surfaces while for the etched surface this feature is essentially narrower and shifted towards higher energies. The maximum at an energy ~0.58 eV related to the transitions between the surface states S_4-S_5, is well resolved for the etched surface, smoothed for the polished surface and revealed only as a shoulder in the spectrum for the ground surface. The feature at ~0.65 eV due to the transitions from the Γ'_{25} valence band maximum and/or from the empty SES *S* to the conduction band bottom or from the filled SES S_4 to the empty SES S_6, is clearly revealed for all the three surfaces under study.

A maximum near 0.9 eV in the loss spectra at E_p=2.0 eV predominates over other maxima for the ground surface while for the polished and etched surfaces this maximum is weaker (Fig. 3 f).

The features at the energies above 1 eV for all the surfaces under investigation at E_p>1.5 eV are broader than the low-energy features. This is due to the fact that these maxima in the loss spectra originate from the electron transitions with participation of states with relatively high energy density (See Table 1).



a b c

d e f

g h

Fig. 3. LEEB energy loss spectra for the ground, polished and etched Ge(111) surfaces at different incident electron energies E_p: *a* – E_p = 0.5 eV; *b* – E_p = 0.75 eV; *c* – E_p = 1.0 eV; *d* – E_p = 1.25 eV; *e* – E_p = 1.5 eV; *f* – E_p = 2.0 eV; *g* – E_p = 2.5 eV; *h* – E_p = 3.0 eV.

Table 1. Energy positions of maxima in the LEEB loss spectra and possible electron transitions.

E (eV), etched surface	*E* (eV), polished surface	*E* (eV), ground surface	Theory (eV) [24–26]	Possible electron transitions
0.35	0.37	0.37		$\Gamma'_{25}-S_7$ $S-S_7$; S_4-S'
0.49	0.45	0.45		$\Gamma'_{25}-S_8$ $S-S_8$
0.57	0.58	0.58		S_4-S_5
0.66	0.65	0.65	0.67	$\Gamma'_{25}-L_1$ $S-L_1$ S_4-S_6
0.74	0.73	0.74	0.74	$\Gamma'_{25}-\Gamma'_2$ $S-\Gamma'_2$
0.82	0.8	0.81		S_4-S_7
0.92	0.90	0.91		S_4-S_8; S_3-S'
1.01	1.00	1.01		S_3-S_5 ; S_4-L_1
1.13	1.13	1.13		S_2-S' ; S_3-S_6 $S_4-\Gamma'_2$
1.26	1.24	1.25	1.25	S_2-S_5 $\Gamma'_{25}-X_1$ $S-X_1$
1.38	1.36	1.35		S_1-S' ; S_2-S_6 L'_3-S'
1.5	1.53	1.51		S_1-S_5 ; S_2-S_8 S_3-L_1 ; L'_3-S_5
1.7	1.75	1.74		S_1-S_6 ; S_2-L_1 L'_3-S_7
2.02	1.96	1.97	2.0 2.07	L'_3-L_1 S_1-L_1 $L'_3-\Gamma'_2$ S_3-X_1
2.38	2.36	2.37		S_2-X_1
2.78	2.76	2.83	2.8	X_4-S' $\Gamma'_{25}-\Gamma_{15}$ $S-\Gamma_{15}$

Notes: 1. Γ'_2, Γ_{15}, Γ'_{25}, L_1, L'_3, X_1, X_4 – high-symmerty points of the reduced Brillouin zone with the density-of-states maxima. 2. S', S – S_8 – SES.

It is worth to notice the behaviour of the features in the spectra in the range 1.70–1.75 eV: at E_p=2.0 eV for all surfaces distinct maxima are observed (Fig. 3 f) while at E_p>2.5eV the maxima in this range are revealed only for the ground and etched surfaces (Fig. 3 g, h). Such behaviour of the features is, in our opinion, the evidence for the fact that surface treatment can modify not only the concentration and energy position of SES, but also the character of the energy dependence of electron transition probabilities. Therefore, it seems practically impossible to relate unambiguously the area under the maxima with the reduced density of the states participating in the electron transition and, moreover, with the concentration of surface states.

4. Conclusions

1. By different treatment of Ge(111) surface one can (a) control the LEEB coefficient value; (b) vary the energy loss intensity due to variation of concentration and energy redistribution of SES as well as energy dependence of electron transition probabilities.

2. Maxima in the energy loss spectra at LEEB clearly correlate with theoretically calculated energy distances between the density-of-states maxima in the valence and conduction bands in the reduced Brillouin zone and surface electron states for the surfaces under investigation.

3. Electron transitions with energy loss below the energy gap value (~0.67 eV) are revealed in the spectra only for E_p<0.75 eV while the states for which the transition energy is higher than 0.67 eV, are revealed in all spectra for E_p>1.0 eV.

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