ELSEVIER

Applied Surface Science 175–176 (2001) 175–180

applied surface science

www.elsevier.nl/locate/apsusc

Evolution of interface excitations under phase transition in two-dimensional layer of Cs on GaAs(1 0 0) and (1 1 1)

V.L. Alperovich*, O.E. Tereshchenko, A.N. Litvinov, A.S. Terekhov

Institute of Semiconductor Physics, Novosibirsk State University, 630090 Novosibirsk, Russia

Accepted 31 August 2000

Abstract

The evolution of electronic excitation spectra under deposition of Cs on the polar GaAs faces (1 0 0) and (1 1 1) with various surface reconstructions is experimentally studied by means of high-resolution electron energy loss spectroscopy (EELS). Similar to the Cs/GaAs(1 1 0) surface studied earlier, for all crystal faces and surface reconstructions we found two energy loss peaks in the band gap of GaAs at Cs coverages exceeding 0.5 monolayer (ML). The analysis of the loss spectra proves that the rise of the loss peaks is due to a phase transition at which dispersed isolated Cs adatoms condense into densely packed clusters, eventually merging in a two-dimensional overlayer with metallic-type excitations. A simple model of plasmon excitations in a metallic layer placed on a dielectric substrate explains qualitatively the essential features of EELS experiments. © 2001 Elsevier Science B.V. All rights reserved.

PACS: 81.15.Ef; 73-40.-c; 68.35Bs

Keywords: Semiconductor; Surface; Adsorption; Alkali metal; Plasmons; EELS

1. Introduction

For the past decades semiconductor surfaces with adsorbed atoms of alkali metals (AM) remain an object of intensive investigations because of interest for fundamental surface science and important applications. Due to a similar electronic structure of various AM with a single electron on the outer shell, AM-semiconductor interfaces were treated as simple model systems for studying the basic features of adsorption [1,2]. Recently both the similarity and simplicity were questioned by experimental and theoretical evidence for strong influence of the interaction between adatoms and effects of electron correlations on the structure and electronic properties of these interfaces. The most complete data are obtained for the nonpolar GaAs(1 1 0) surface with cesium overlayers. In particular, low-dimensional structures of Cs adatoms, such as regular one-dimensional chains at low coverages and ordered two-dimensional clusters at coverages $c > 0.5$ monolayers (ML) were observed on the cleaved GaAs(1 1 0) surface by scanning tunneling microscopy (STM) [3]. DiNardo et al. [4] showed that the formation of the two-dimensional clusters was accompanied by the rise of intense peaks with energies $E \approx 0.4$ eV (peak L1) and 1 eV (peak L2) in the electron energy loss spectra. It was suggested in [4] that the emergence of these peaks was closely related to the formation of the Mott–Hubbard insulator state arising as a result of Coulomb correlation in the

* Corresponding author. Tel.: +7-3832-357508; fax: +7-3832-351771.

0169-4332/01/$ – see front matter © 2001 Elsevier Science B.V. All rights reserved.
PII: S0169-4332(01)00058-7

system of two-dimensional electrons. For GaAs(1 1 0) this idea was theoretically substantiated by Pankratov and Scheffler [5]. Later Pennino et al. [6] compared loss spectra measured with various AMs (Na, K, Rb, Cs) deposited on GaAs(1 1 0) and found a song correlation between the position of the L1 and L2 peaks observed at submonolayer coverages with the energy of surface plasmons in the respective metal. It was also shown in [6] that at low temperatures, under deposition of AM above 1 ML, the peak L2 evolved into a broad band corresponding to the excitation of surface plasmons in the AM. These results support an alternative picture for the structure and electronic properties of such a surface. This picture involves the formation of two-dimensional clusters of adatoms with the metallic excitation spectrum. In [6] L2 loss was attributed to the excitation of plasmons localized in Cs clusters. However, the evolution of the loss spectra under increasing coverage and the origin of L1 loss remained unclear. To clarify further the picture of the formation of interfaces between alkali metal adatoms and semiconductors, the evolution of the electronic excitation spectrum under deposition of Cs on the polar GaAs faces (1 0 0) and (1 1 1) with various surface reconstructions is experimentally studied in this work by means of high-resolution electron energy loss spectroscopy (EELS). The results show the universal behavior of the spectra obtained for different Cs/GaAs surfaces and support the interpretation of the loss peaks as being due to excitation of localized plasmons in cesium overlayer. Preliminary results were published in [7].

2. Experimental

The experiment was done on Zn-doped *p*-GaAs layers grown by liquid phase epitaxy on GaAs substrates with (1 0 0), (1 1 1)A and (1 1 1)B orientations. The concentration of holes was equal to 1×10^{18} cm^{-3}. Atomically clean and structurally ordered GaAs surface was prepared by removing the oxides in the solution of HCl in isopropyl alcohol in dry nitrogen atmosphere, transferring the sample in a hermetically sealed container without air contact into electron spectrometer ADES-500, with subsequent heating in ultra-high vacuum [8]. The base pressure in the analytical and preparation chambers of the spectrometer was 3×10^{-11} and 8×10^{-11} mbar, respectively. The surface structure and composition were determined by low-energy electron diffraction (LEED) and X-ray photoelectron spectroscopy (XPS). Cesium deposition and all measurements were performed at room temperature. The coverage c of the Cs layer was determined from the dependence of the $Cs3d_{5/2}$ photoemission peak area on the deposition time (dose). As the dose increased, the area of the peak, which is proportional to Cs amount on the surface, also increased and then saturated. The effective thickness of Cs layer corresponding to the saturated value of the area was taken as one monolayer, $c = 1$ ML. EELS spectra were measured at incident electron energy $E_i = 15$ eV with total energy resolution better than 90 meV and angular resolution of 1°.

3. Results and discussion

In the present experiment we deposited Cs on the clean As-stabilized GaAs(1 0 0)$-(2 \times 4)/c(2 \times 8)$ surface, Ga-stabilized GaAs(1 0 0)$-(4 \times 2)/c(8 \times 2)$ $-(4 \times 2)/c(8 \times 2)$ surface, on the surface with intermediate reconstruction (1 0 0)$-(3 \times 1)/(3 \times 6)$, and on other crystal faces, namely, GaAs(1 1 1)A$-(2 \times 2)$ and GaAs(1 1 1)B$-$ (1×1). For all surfaces under Cs deposition we observed gradual blurring of the LEED spots and increase of the diffuse background. On the As-stabilized surface GaAs(1 0 0)$-(2 \times 4)$ the increase of the background and broadening of the spots were observed starting from $c \approx 0.1$ ML; at $c \approx 0.5$ ML the LEED picture completely vanished. The lack of order on Cs/GaAs(1 0 0)$-(2 \times 4)/c$ (2×8) surface was directly observed in [9] by STM. The Ga-stabilized $(4 \times 2)/c(8 \times 2)$ surface reconstruction was found to be more stable with respect to Cs deposition. For coverages up to $c \leq 0.3$ ML no degradation of the LEED pattern was observed, in agreement with the results of [10]. The reconstruction $(4 \times 2)/c(8 \times 2)$ was observed up to $c \approx 0.75$ ML; it transformed to disordered (1×1) only at $c \approx 1$ ML. Under Cs deposition on GaAs(1 1 1)A$-(2 \times 2)$ the reconstruction (2×2) gradually transformed in (1×1) at $c \approx 0.3$–0.5 ML; the picture completely vanished at $c \approx 1$ ML. The Cs/GaAs(1 1 1)B$-(1 \times 1)$ LEED picture gradually degraded with increasing coverage and vanished at $c \approx 1$ ML.

The evolution of the electron energy loss spectra under deposition of Cs on the Ga-stabilized GaAs(1 0 0)$-(4\times 2)/c(8\times 2)$ surface is shown in Fig. 1 by six lower curves denoted by circles. It is seen that on the clean surface there are no losses in the band gap of GaAs $E_g = 1.42$ eV; interband transitions are observed in the energy range $E > E_g$. With the increase of coverage up to 0.5 ML, the increase of losses in the interband region and the shift of the loss threshold towards lower energies were observed. At $c \approx 0.5$ ML two loss peaks abruptly appeared in the band gap region at $E \approx 05$ eV (peak L1) and $E \approx 1.1$ eV (peak L2). These peaks increased rapidly with further increase of c and then saturated. Similar changes occurred in the loss spectra under Cs deposition on all crystal faces and surface reconstructions studied in the present work. For comparison, three upper curves in Fig. 1 show the loss spectra at monolayer coverages of Cs deposited on GaAs(1 0 0) $-(2\times 4)/c(2\times 8)$, GaAs(1 1 1)A$-(2\times 2)$ and GaAs (1 1 1)B$-(1\times 1)$. It is seen that the shapes of the spectra are quite similar.

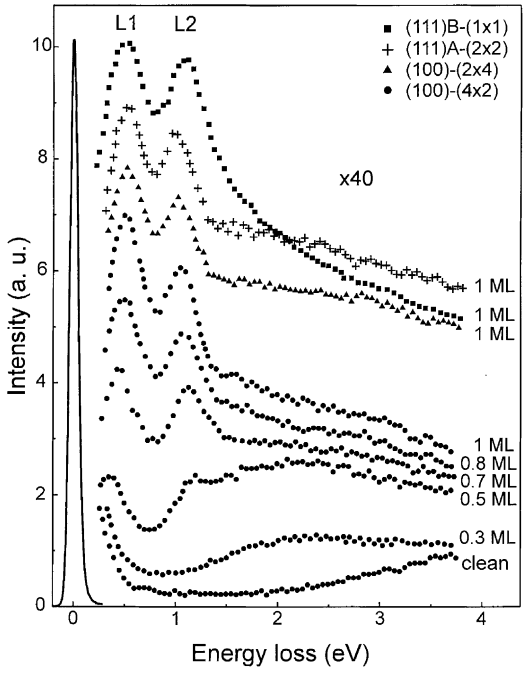

Fig. 1. Evolution of EELS spectra under Cs deposition on the Ga-stabilized GaAs(1 0 0)$-(4\times 2)$ surface is shown by six lower curves denoted by circles. For comparison EELS spectra of GaAs(1 0 0)$-(2\times 4)$, GaAs(1 1 1)A$-(2\times 2)$, and GaAs(1 1 1)-B$-(1\times 1)$ surfaces at monolayer Cs coverages are shown by three upper curves. For clarity the spectra shown by triangles, crosses and squares are shifted upward by 2.5, 3.5 and 3.5 units, respectively. All spectra are measured in the specular reflectance geometry with the incidence and scattering angles equal to 55°.

To determine the evolution of the position, intensity and width of the observed losses, the spectra were decomposed into L1 and L2 peaks plus a broad band centered around $E \approx 2$ eV. Fig. 2 shows the dependence of the intensities of L1 and L2 peaks on the Cs coverage for the Ga-stabilized GaAs(1 0 0)$-(4\times 2)/c(8\times 2)$ and As-stabilized GaAs(1 0 0)$-(2\times 4)/c(2\times 8)$ surfaces. A threshold increase of the intensities is observed for both peaks at $c \leq 0.5$ ML. It is seen that the dependences for both surfaces are the same within the experimental error. This was also true for the other surfaces studied here. The positions and widths of the peaks did not depend on coverage within 10%.

Similar to the results obtained earlier for Cs/GaAs(1 1 0) [4], the measurements of the loss spectra at a fixed incident angle and various scattering angles showed no substantial dispersion: the positions of both peaks remained constant within 10%. On the other hand, we observed a strong angular dependence of the relative intensities of peaks L1 and L2. Fig. 3 shows EELS spectra measured at various angles in the specular reflectance geometry after deposition of 0.7 ML of Cs on GaAs(1 1 1)A$-(2\times 2)$. It is seen that the intensity of the peak L2 is higher for larger

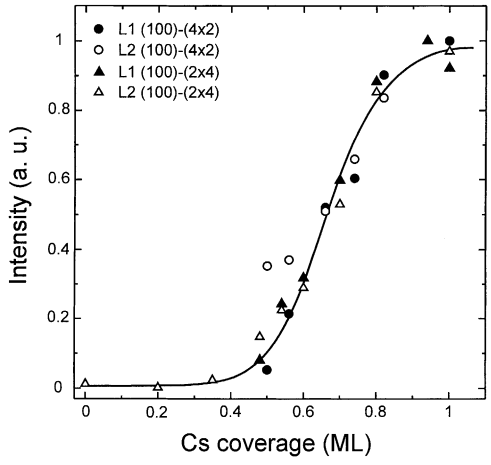

Fig. 2. The intensities of L1 and L2 losses as a function of coverage for Cs deposition on GaAs(1 0 0)$-(4\times 2)$ and GaAs(1 0 0)$-(2\times 4)$.

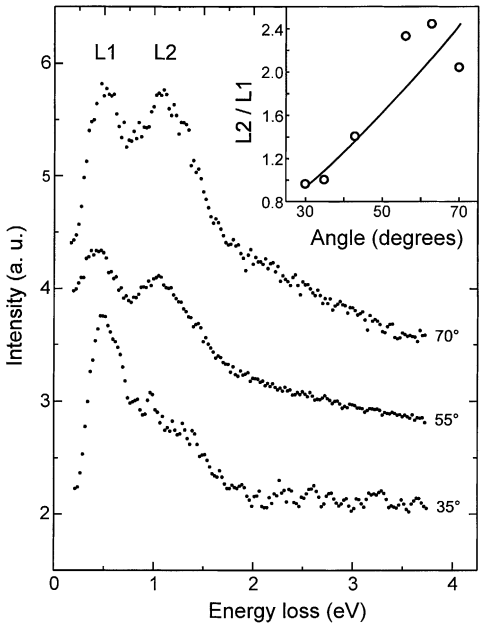

Fig. 3. EELS spectra measured at various angles in the specular geometry after deposition of 0.7 ML of Cs on GaAs(1 1 1)-A$-(2\times 2)$. For clarity the spectra measured at 55 and 70° are shifted upwards by 2.5 units. The inset shows the ratio of the intensity of L2 loss to the intensity of L1 loss as a function of the angle.

angles, i.e. for more glancing incidence. The inset shows the ratio of intensities of peaks L2 and L1 as a function of angle. With the angle increasing from 30 to 75°, the intensity ratio increases more than twice.

The similarity of the loss spectra measured earlier in [4,6] at Cs/GaAs(1 1 0) and in the present work at Cs/GaAs surfaces with different faces and surface reconstructions proves that the formation of electron excitation spectra of Cs/GaAs interfaces has universal features, despite substantial differences in the structure and electronic properties of the initial clean surfaces. It can be inferred that the appearance of the loss peaks L1 and L2 on all GaAs surfaces studied here, just as on Cs/GaAs(1 1 0) surface, is due to a phase transition, which can be explained similar to the case of AM deposited on the metal substrates [11–16]. At low coverages the electrostatic repulsion between the adatom-induced microdipoles should keep the adatoms uniformly dispersed. At increasing coverage, the decrease of the mean distance between adatoms and partial depolarization of the surface dipoles facilitate overlapping of the valence electron wave functions of adjacent adatoms. At a critical coverage the repulsion changes to attraction due to the direct cohesive force. Therefore, dispersed adatoms start to be condensed and form two-dimensional islands. This condensation is considered to be a first order phase transition, which is characterized by discontinuity of the chemical potential and by coexistence of two phases [12]. Although direct STM study is available only for As-stabilized Cs/GaAs(1 0 0)$-(2\times 4)/c(2\times 8)$ surface [9], the existence of two-dimensional Cs clusters on Ga-stabilized surface was indirectly confirmed by photoreflectance spectroscopy [17].

In [4] the condensed phase formed on Cs/GaAs(1 1 0) at $c > 0.5$ ML was assumed to be a Mott–Hubbard insulator, L1 loss was interpreted as a transition over the Hubbard gap, and L2 loss — as a transition in the Cs–Ga complex. Alternatively, correlation between the positions of the loss peaks with the energy of surface plasmons for various AM [6] and similarity in the dose behavior of the peaks observed in the present work suggest that the loss peaks L1 and L2 have a similar origin and are related to the excitation of localized plasmons in Cs islands, which have a metallic rather than insulating spectrum. However, the origin of plasmons responsible for the loss peaks on Cs/GaAs surface is still not clear in detail. To elucidate the origin of these plasmons we considered a simple model of a metallic layer with thickness d placed on a substrate with a dielectric constant ε_s. The calculations were done in the same manner as for the plasmons in a metallic slab in vacuum [18], except that in the boundary conditions the presence of the dielectric medium on one side of the metal layer was taken into account. The lateral dispersion $\omega(q)$ of the two types of plasmons is shown in Fig. 4. Here q is the lateral wave vector. In the long wavelength limit ($qd \ll 1$) the lower branch 1 corresponds to the longitudinal plasma oscillations with the dispersion $\omega \propto \sqrt{q}$ characteristic of the two-dimensional plasmons [18], and the upper branch 2 corresponds to the transverse oscillations with the frequency approaching the bulk plasmon frequency ω_p. In the short wavelength limit ($qd \gg 1$) the lower branch approaches the frequency of plasmons localized on the interface between the metal and dielectric substrate $\omega_{int} = \omega_p/\sqrt{\varepsilon_s + 1}$, while the upper branch approaches the frequency of plasmons localized on the surface of

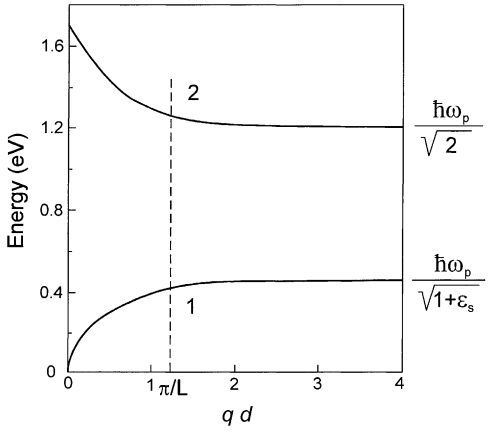

Fig. 4. The calculated dispersion of plasmons in a metallic layer with thickness d placed on a dielectric substrate. The energy $E_p = 1.7$ eV of bulk plasmons in the metal is assumed. The vertical dashed line denotes the wave vector of a plasmon localized in a metallic island with lateral dimension L.

the AM metal $\omega_{surf} = \omega_p/\sqrt{2}$. With the dielectric constant of GaAs $\varepsilon_s = 12.9$, the ratio $\omega_{surf}/\omega_{int} = 2.6$ is close to the ratio of experimental energy positions of L2 and L1 peaks $E_{L2}/E_{L1} = 2.2$. Therefore, we tentatively associate L1 and L2 peaks with the excitation of plasmons corresponding to the lower and upper branches, respectively. Due to lateral localization in Cs islands, plasmons corresponding to non-zero values of $q \approx \pi/L$ are excited in EELS experiment, where L is the lateral dimension of an island.

To reach an agreement between the calculated and experimental values of the peak positions, one has to assume $\hbar\omega_p = 1.7$ eV, which is considerably smaller than the energy of plasmons in bulk cesium which is equal to $\approx$3 eV. This discrepancy can be partly explained by the electron charge transfer from the Cs adatoms to the surface atoms of GaAs. The charge transfer partially depletes s-band of Cs and thus leads to a decrease of plasmon frequencies. The simple model of a metallic layer explains the essential features of the low-temperature experiments [4,6] with deposition of Cs above 1 ML: with increasing thickness of Cs layer the L2 peak was shifting to the frequency of surface plasmon of cesium, while L1 peak was gradually vanishing due to the increased screening of the interaction between incident electrons and interface plasmons. The model is also in a qualitative accord with the observed angular dependence of EELS spectra. Due to electrostatic repulsion, probe electrons in the layer are pushed by an incident electron preferentially in the direction perpendicular to its trajectory. Thus, at glancing incidence the transverse plasmons are more readily excited as compared to the longitudinal plasmons. This explains the observed increase of the relative intensity of L2 loss with increasing angle (see Fig. 3).

The question is why the plasmon L1 and L2 losses are not distinctly observed on other AM/semiconductor and AM/metal surfaces. A possible answer is that the observation of narrow resonances corresponding to the overlayer plasmons is favorable on Cs/GaAs surface because these resonances fall in the bulk band gap. In contrast, on AM/metal surfaces plasmons are in resonance with the continuum of bulk states and are strongly broadened. The broadening may take place on semiconductor substrates if the plasmon energy is larger than the band gap. Besides, on AM/metal surfaces the longitudinal plasmons are effectively screened by conduction electrons and thus should be suppressed in the loss spectra. The observation of longitudinal (intraband) plasmons was reported earlier for the K/Si(1 1 1) surface, where it revealed as a weak shoulder on the low-energy side of the EELS peak corresponding to the transverse (interband) plasmon [14]. Various types of plasmons were also observed on Cs/Si(1 0 0) surface by photoelectron spectroscopy [19].

To describe quantitatively the observed loss spectra, a theory should be used, which takes into account rigorously the chemical nature of the semiconductor and AM, and also electron–electron correlation effects. It should be noted that unlike Cs/GaAs(1 1 0), the surfaces studied in this work are disordered at 1 ML Cs coverages. Therefore, it is not appropriate, strictly speaking, to describe elementary surface excitations by a dispersion law. In a comprehensive theory the AM/GaAs surface should rather be considered as a two-dimensional "granular metal", in other words, as a disordered "effective" medium [20] with electrically coupled plasmon oscillations in a randomly distributed array of two-dimensional metallic islands of adatoms.

In conclusion, it was experimentally shown that the electron energy loss spectra of Cs/GaAs surfaces are similar for various crystal faces and reconstructions.

Intense loss peaks, which appear in the band gap at coverages above 0.5 ML, are due to the phase transition from dispersed gas of adatoms to densely packed two-dimensional islands. These peaks correspond to the excitation of plasmons localized in Cs islands. Thus, at coverages above 0.5 ML, the surface of Cs/GaAs is a ''granular'' metal rather than Hubbard insulator.

Acknowledgements

We would like to thank M.V. Entin and A.O. Govorov for discussions and helpful remarks, and N.S. Rudaya for growing the epitaxial GaAs layers. This work was supported by the Federal program ''Surface atomic structures'' (Grant 4.4.99) and by the program ''Integration'' of the Ministry of Education of the Russian Federation via the Novosibirsk State University (Project No. 274).

References

[1] M. Prietsch, M. Domke, C. Laubschat, T. Mandel, C. Xue, G. Kaindl, Z. Phys. B 74 (1989) 21.
[2] F. Bechstedt, M. Scheffler, Surf. Sci. Rep. 18 (1993) 145.
[3] L.J. Whitman, J.A. Stroscio, R.A. Dragoset, R.J. Celotta, Phys. Rev. Lett. 66 (1991) 1338.
[4] N.J. DiNardo, T.M. Wong, E.W. Plummer, Phys. Rev. Lett. 65 (1990) 2177.
[5] O. Pankratov, M. Scheffler, Phys. Rev. Lett. 70 (1993) 351.
[6] U. Pennino, R. Companò, B. Salvarini, C. Mariani, Surf. Sci. 409 (1998) 258.
[7] O.E. Tereshchenko, V.L. Alperovich, A.S. Terekhov, A.N. Litvinov, JETP Lett. 70 (1999) 550.
[8] O.E. Tereshchenko, S.I. Chikichev, A.S. Terekhov, J. Vac. Sci. Technol. A 17 (1999) 2655.
[9] J. Kim, M.C. Gallagher, R.F. Willis, Appl. Surf. Sci. 67 (1993) 286.
[10] B. Goldstein, Surf. Sci. 47 (1975) 143.
[11] T. Aruga, Y. Murata, Progr. Surf. Sci. 31 (1989) 61.
[12] G.M. Watson, P.A. Brühwiler, H.J. Sagner, K.H. Frank, E.W. Plummer, Phys. Rev. B 50 (1994) 17678.
[13] M. Nakayama, T. Kato, K. Ohtomi, Solid State Commun. 50 (1984) 409.
[14] T. Aruga, H. Tochihara, Y. Murata, Phys. Rev. Lett. 53 (1984) 372.
[15] A. Liebsch, Phys. Rev. Lett. 67 (1991) 2858.
[16] S.R. Barman, K. Horn, P. Haberle, H. Ishida, A. Liebsch, Phys. Rev. B 57 (1998) 6662.
[17] D. Paget, B. Kierren, R. Houdré, J. Vac. Sci. Technol. A 16 (1998) 2350.
[18] A.V. Chaplik, Surf. Sci. Rep. 5 (1985) 289.
[19] Y.-C. Chao, L.S.O. Johansson, R.I.G. Uhrberg, Phys. Rev. B 56 (1997) 15446.
[20] M.V. Entin, JETP 114 (1998) 669.