Diffusion and ordering of Cs adatoms on GaAs(001) studied by reflectance anisotropy spectroscopy

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Diffusion and ordering of Cs overlayers deposited at a low temperature of 90 K on GaAs(001) are observed by reflectance anisotropy (RA) spectroscopy after annealing to higher temperatures. At low coverages (≤ 0.3 monolayer), the ordering of cesium is revealed as a narrowing of the Ga-dimer line in the RA spectra, which occurs after annealing at $T \geqslant 200$ K. A possible reason for such ordering is the diffusion of individual adatoms to preferential adsorption sites. At coverages larger than 0.5 monolayer, for which the majority of adatoms are not isolated, the diffusion-induced changes of RA spectra occur at a temperature lower than 200 K and are characterized by a broad spectrum, which suggest a change of the surface macroscopic anisotropy. [S0163-1829(97)50548-0]

After decades of intensive investigations, alkali metals on semiconductors are still a model system for studying structural and electronic properties of adsorbate-semiconductor interfaces.[1,2] In particular, low-dimensional ordered structures of Cs adatoms, such as regular 1D chains and 2D clusters, were observed at room temperature (RT) on the cleaved GaAs(110) surface by scanning tunneling microscopy (STM).[3] An important prerequisite for the formation of ordered structures is the diffusion of adatoms along the surface.[4–6] In Ref. 6 it was shown that Cs diffusion on Si(001) is allowed only at temperatures exceeding 300 K, but the situation for GaAs is less clear. The observation of ordered structures on GaAs(110) (Ref. 3) proves that the diffusion of cesium adatoms is allowed at RT. For the practically important GaAs(001) surface, no ordered structures of Cs adatoms were observed at RT by STM and electron diffraction techniques.[7,8] This may indicate either the absence of the adatom diffusion, or, quite contrary, the blurring of the STM picture by intensive motion of adatoms along the surface.

Recently, reflectance anisotropy (RA) spectroscopy proved to be very useful for studying clean and adsorbate-covered semiconductor surfaces.[9–15] This technique consists of measuring the reflectivity difference for light linearly polarized along the $[1\bar{1}0]$ and $[110]$ directions of the surface. RA spectra of the GaAs(001) surface contain peaks corresponding to anisotropic optical transitions involving electronic states of gallium and arsenic dimers.[9,11]

Here RA spectroscopy was applied to studying the diffusion and ordering of Cs adatoms on Ga-rich GaAs(001). We deposited cesium at a low temperature (LT) of 90 K, which, because of the absence of surface diffusion, produced a disordered adlayer. Subsequently, annealing to progressively increasing temperatures up to 360 K was performed. The onset of surface diffusion at a given temperature changed the distribution of Cs adatoms with respect to surface Ga dimers.

Consequently, the RA spectrum was changed. Unlike macroscopic probes, which were used in most previous studies,[5,6] the present technique is sensitive to adatom motions over microscopic distances.

We have used a molecular-beam-epitaxy (MBE) grown arsenic-capped UP$^+$ GaAs structure,[16] which consisted of a 100-nm undoped GaAs layer grown on top of a 1000-nm highly doped p layer. The experimental setup, situated at Ecole Polytechnique, has been described elsewhere.[11] It consists of an ultrahigh vacuum system with a base pressure in the low 10^{-11} mbar range. Using both cooling with liquid nitrogen and heating with a tungsten filament, the temperature of the sample holder could be changed between 90 and 870 K. For the isochronal anneals used here, the temperature of the sample was monitored by measuring photoreflectance spectra[16,17] and using the known temperature dependence of the band gap.[18] After insertion into vacuum, the protective arsenic overlayer was removed by heating to 810 K, which revealed the gallium-rich surface. Cesium deposition was performed on the sample cooled to $T=90$ K, using a thoroughly outgassed cesium getter. Calibration of the cesium coverage for a given exposure was performed using Auger spectroscopy.[15] After each experiment, the sample was annealed to 820 K in order to desorb the cesium without damaging the surface.

The RA spectrum measured at LT on the clean surface is shown by curve a in Fig. 1. This spectrum is characteristic of the gallium-rich GaAs(001) surface.[9,10,15] Although the origin of the anisotropy of this surface is not quantitatively understood at the present time, the dominant peak at photon energy $\hbar\omega=2.3$ eV can be qualitatively assigned to the anisotropic optical transition involving localized states of Ga dimers. The high-energy satellite, which is revealed as a shoulder near $\hbar\omega=2.6$ eV, is interpreted as due to a distinct gallium dimer in the unit cell. No contribution due to As dimers is observed near $\hbar\omega=3$ eV.
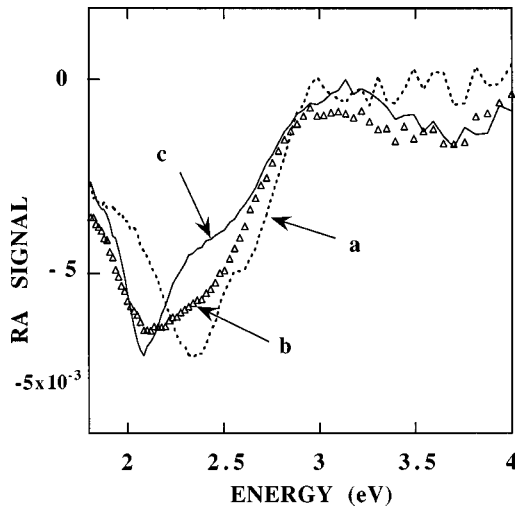
FIG. 1. Reflectance anisotropy spectra measured at low temperature $T = 90$ K on the clean surface of GaAs(001) (curve a), immediately after deposition of 0.3 ML of cesium (b), and after subsequent anneal of the Cs overlayer at 310 K (c).
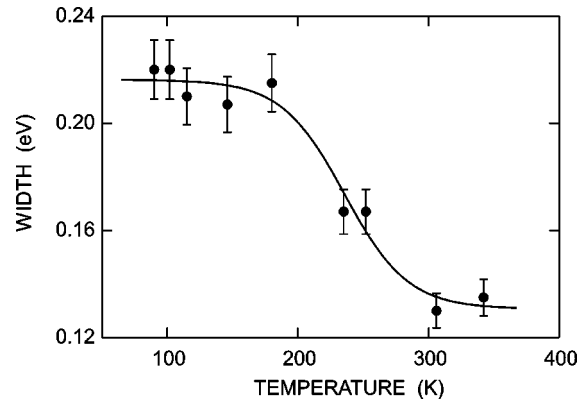

FIG. 2. The dependence of the width of the leading Ga-dimer peak in RA spectra on the temperature of isochronal anneals of 0.15 ML Cs overlayer deposited at $T = 90$ K. The solid line is drawn to guide the eye.

Curve b of Fig. 1 shows the RA spectrum taken after LT deposition of 0.3 ML of cesium. Both Ga-dimer lines shift to lower energies by 0.3 eV, and the spectrum substantially broadens.[14,15] A new line arises at $\hbar\omega = 3.6$ eV; its origin will be discussed elsewhere. The exact reason for the monotonic low-energy shift of RA lines with increasing Cs coverage has not been clarified so far. We believe that it can be qualitatively explained as a nonlocal electrostatic effect caused by the averaged influence of the adatom-induced surface microdipoles on the orbitals involved in the surface optical transition. The observed inhomogeneous broadening of the spectrum is due to potential fluctuations created by the random distribution of Cs adatoms deposited at low temperature.

The RA spectrum measured after annealing the LT-deposited Cs overlayer to room temperature and after cooling it back to LT is shown by curve c in Fig. 1. Comparison of curves b and c shows that annealing produced a substantial modification of the RA spectrum. The position of the Ga dimer line did not change, but the line became much narrower, and its integrated intensity somewhat reduced. A similar effect was observed at smaller coverage $\theta = 0.15$ ML. Since the spectra before and after anneal were measured at the same temperature of 90 K, and since it was verified by Auger spectroscopy that cesium does not desorb at RT,[19] the only possible explanation for this irreversible modification of the adatom overlayer is the surface diffusion of cesium. Evidently, the diffusion transforms the cesium overlayer from a disordered state with randomly distributed adatoms and large potential fluctuations, which inhomogeneously perturb the dimer states, into an ordered state with a reduced magnitude of potential fluctuations.

In principle, the driving force for this disorder-order transition could be the repulsive dipole interaction,[5,6] which might eventually lead to a two-dimensional hexagonal lattice of adatoms. However, it is difficult to explain the reduction of the local disorder at the Ga dimer position by this mechanism, since such lattice is not expected to be correlated with the substrate. It is more likely that the GaAs substrate im-

poses its own order to the structure of the adsorbate layer, so that the ordering is due to the diffusion of adatoms to preferential sites in the unit cell. Since these sites are situated regularly with respect to the Ga dimers, their occupation can indeed reduce the inhomogeneous broadening of the RA spectra. The reason for the decrease of the integrated intensity of the Ga-dimer line is not yet clear. It is possible that the observed quenching of the line is due to a decrease of the oscillator strength of the optical transition, or to partial occupation of its final state due to electron charge transfer from cesium.

To determine the temperature range in which the disorder-order transition occurs, we performed isochronal 20-min anneals of the LT-deposited Cs layer at progressively increasing temperatures. In this experiment we used a smaller Cs coverage $\theta = 0.15$ ML, which corresponds to approximately one cesium atom per (4×2) unit cell. To exclude the effect of thermal broadening of the spectral lines, after each anneal at a given temperature, the sample was cooled down, and the RA spectrum was measured at $T = 90$ K. The width Γ of the leading Ga-dimer peak was determined phenomenologically, by fitting the experimental spectrum by a sum of Gaussian lines.

The dependence of Γ on the annealing temperature is shown in Fig. 2. It is seen that the transition occurs in the 200–300 K temperature range. In this range the width Γ drops by a factor of 1.6, while at lower and higher temperatures it does not change within experimental error. To estimate the corresponding activation energy E_d of the adatom diffusion, one can use the following expression:[4]

$$D = D_0 \exp(-E_d/kT), \qquad (1)$$

where $D = l^2/\tau$ is the diffusion coefficient, τ is the duration of the anneal, and l is the diffusion length, which is sufficient for the transition to the ordered state. For estimation l can be taken of the order of the dimension of the surface unit cell $l \approx 1$ nm. Expressing the pre-exponential factor $D_0 = a_0^2 \nu$ through the interatomic distance on GaAs(001) surface $a_0 = 0.4$ nm and characteristic phonon frequency $\nu \approx 10^{13}$ Hz, we obtain $E_d \approx 0.7$ eV for the temperature of the transition $T_c = 235$ K. A smaller value of 0.47 eV was obtained in Ref. 6 for Cs on Si(001). This difference may be due to the polar
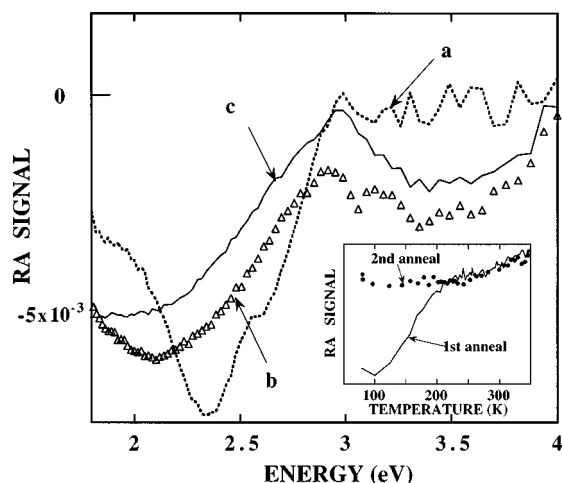
FIG. 3. Reflectance anisotropy spectra measured at low temperature $T = 90$ K on the clean surface of GaAs(001) (curve a), immediately after deposition of 0.8 ML of cesium (b), and after subsequent anneal of the Cs overlayer at 360 K (c). In the inset, the temperature dependence of the RA signal at $\hbar\omega = 2.1$ eV is shown for the first and second anneals.

nature of the GaAs surface, which generates microscopic in-plane electric fields on the surface and, thus, hinders the adatom diffusion.

Comparison of curves a and c of Fig. 1 shows that, surprisingly, the width of the Ga-dimer line after the anneal is even smaller than at the clean surface. This suggests that diffusion of cesium leads to the effective screening of the potential fluctuations created both by randomly deposited adatoms and by initially charged centers, which are present on the clean surface. Such an improvement of the surface electronic properties under Cs deposition is similar to previously observed cesium-facilitated unpinned behavior of the Fermi level on GaAs(001) surface.[17]

The results presented here are in accordance with the previous observation of the increase of the amplitude of the Ga dimer line under room temperature deposition of cesium on a similar GaAs(001) surface.[15] It has been proposed in Ref. 15 that this increase at small doses was due to the diffusion of Cs adatoms to some energetically favorable adsorption sites. The annealing experiments performed in the present study enabled us to separate the processes of deposition and diffusion of Cs adatoms, and, thus, directly prove this hypothesis.

For large coverages $\theta \geqslant 0.5$ ML, at which cesium adatoms can no longer be considered as isolated, both the effect of diffusion and its characteristic temperature are in sharp contrast with the corresponding behavior found at $\theta < 0.5$ ML. Shown in Fig. 3, are the RA spectra of the clean surface (curve a) and immediately after LT deposition of 0.8 ML of Cs (curve b). One sees that the Ga-dimer peak evolves into a broad band which does not change its position and shape at increasing θ.[15] At these large coverages, the initially localized states of gallium dimers are strongly perturbed and mixed with the states of the cesium layer. Therefore, the observed RA spectra can be assigned to transitions between the bands of these mixed states rather than local optical transitions in individual dimers.

Shown by curve c of Fig. 3 is the spectrum taken after annealing to RT and subsequent cooling to LT. Comparing

curves b and c, one sees that the width of the spectral band does not decrease. On the other hand, the change of the RA signal extends over the whole energy range. Such a broad spectrum is obviously not due to surface dimers, but can be explained by a macroscopic anisotropy[20] induced, for example, by steps which are known to appear preferentially along the $[1\bar{1}0]$ direction.[21] A possible explanation of the modification of the macroscopic anisotropy is the "decoration" of these steps by Cs adatoms, which changes the dielectric constant for light polarized along the steps. Another possible option may be the formation of one-dimensional adatom structures, similar to the ones predicted for the K/GaAs(001) system.[22]

In the same way as for the low coverage regime, the temperature range in which the reorganization takes place can be determined by annealing the surface. However, as for large coverages the RA spectra are broad, and the modification of their shape with increasing temperature is almost entirely due to cesium diffusion, it is sufficient to monitor the magnitude of RA signal *during* the first anneal from LT to RT, without performing isochronal anneals at intermediate temperatures. Shown in the inset to Fig. 3 are the temperature dependences of the RA signal measured at $\hbar\omega = 2.1$ eV during the first and the second anneal after LT deposition. Indeed one sees no change during the second anneal, which further shows that all the relevant cesium diffusion occurs in an irreversible way during the first anneal. For the first anneal, the RA change occurs in the range of $T = 120$–200 K, that is at temperatures significantly lower than for the diffusion of individual adatoms. This temperature range corresponds to a smaller activation energy for the diffusion $E_d \approx 0.5$ eV.

It is generally admitted that the decrease of activation energy with increasing coverage reveals repulsive lateral interactions between adatoms.[5,6] The relative role of the cesium-cesium interaction with respect to the cesium-substrate interaction increases with coverage because at $\theta > 0.5$ ML most adatoms are embedded in cesium two-dimensional clusters. Under anneal to RT, the diffusion restructuring of the adlayer is governed by the disruption of large clusters into smaller ones.[23] The driving force for the disruption may be due to the electrostatic interaction between dipoles, or to strains in the adsorbed layer, since the cesium atomic radius is larger than half of the distance between possible adsorption sites.

In conclusion, we show that the change of the shape of the RA spectra can be used to study the diffusion and ordering of Cs adatoms deposited on GaAs(001) at low temperature, under annealing to higher temperatures. As a function of Cs coverage, two distinct regimes are found. At low coverages, diffusion of individual atoms leads to ordering of the adlayer, which is revealed as a narrowing of the Ga dimer line. At large coverages, the restructuring of the adlayer results in a change of the surface macroscopic anisotropy, and is characterized by a reduced activation energy.

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