Optical properties of magic clusters formed in both reactive and non-reactive systems

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Magic clusters are the smallest ordered quantum dots; hence, they represent promising materials for optoelectronics. However, their optical properties still have not been studied. Therefore, the purpose of this work is investigation of optical properties of magic clusters formed both in reactive (Cr/Si(111)) and non-reactive (In/Si(111)) systems. The ‘adsorbate-silicon’ system named ‘reactive’, if reactions resulting in silicide(s) formation take place in it. Using differential reflectance spectroscopy, optical functions of Indium and Chromium magic clusters were obtained. Having analyzed obtained spectra, we conclude that Cr magic clusters are CrSi islands and Si surface covered by In magic clusters is a semiconductor. A new method of obtaining saturation coverage of studied surface structures was proposed. [DOI: 10.1390/ejssnt.2006.650]

Keywords: Indium; Chromium; Optical spectroscopy; Silicon; Quantum dots; Optical properties; Differential reflectance spectroscopy

I. INTRODUCTION

Magic clusters are the smallest ordered quantum dots; for this reason they represent promising materials for optoelectronics. However, their optical properties still have not been studied. Formation of magic clusters (MC) in reactive systems [1] differs from those in non-reactive ones [2] (‘adsorbate-silicon’ system is named ‘reactive’, if reaction resulted in silicide(s) formation takes place in it). The resulting compounds can differ in optical and conducting properties. For this reason the purpose of this work is investigation of optical properties of MC formed both in reactive (Cr/Si(111)) and non-reactive (In/Si(111)) systems. The choice (In/Si(111) and Cr/Si(111) systems) is explained by formation of MC at relatively low temperature (100°C) in these systems. In order to further decrease the temperature of MC formation, we reduced the deposition rate.

In this work, we report the results on optical properties of Indium and Chromium MC obtained by differential reflectance spectroscopy (DRS) that is a powerful in situ method. Using a new method of DRS data processing, named ‘the method of dynamic standard’, we can obtain the optical function of these MC for the first time.

II. EXPERIMENTAL DETAILS

The experiments were carried out in two ultra high vacuum (UHV) chambers: ‘Varian’ (base pressure 2 × 10⁻⁸ Pa) and ‘Omicron’ (base pressure 1 × 10⁻⁸ Pa). The former is equipped with Auger electron spectroscopy (AES), DRS, low energy electron diffraction (LEED). The latter is equipped with AES, scanning tunneling microscopy (STM) techniques. AES and LEED were used for estimation of film composition and surface periodicity. The data obtained by these methods are auxiliary, they are not presented in the article. The samples were cut from n-type Si(111) wafer (7.5 Ω·cm) and cleaned by toluene before insertion into the sample holder. The initial Si(111)7×7 surface was prepared by flash cleaning, i.e. the sample was outgassed at 500°C for several hours and then heated at 1250°C for a few seconds. RT deposition of indium and chromium atoms on silicon was performed from tantalum tubes. The deposition rate measured by quartz microbalance sensor was 0.05 ML/min (1 ML (monolayer)= 7.8 × 10¹⁴ atoms/cm²) and 0.01 nm/min, respectively.

The DRS technique has been described in [3]. The experimental value obtained either during DRS study or after the experiments have been finished is differential reflectance coefficient (DRC)

\[ \frac{\Delta R}{R} = \frac{R_n(h) - R_0}{R_0} \]

where \( R_0 \) and \( R_n(h) \) are the substrate reflectance before deposition (i.e. Si(111)7 × 7) called “standard” in DRS and after formation of a film having the thickness \( h \), respectively. The DRC spectra were recorded by multichannel analyzer having 3684 photodiodes. The spectral range extended from infrared (0.8 eV) up to visible light (2.8 eV). The sample was illuminated by unpolarized light, the incidence angle was 17°. The obtained DRC spectra contain information about optical properties of all components the film contains. When DRC is proportional to the film thickness Aspnes and McIntyre equation [4] can be applied to obtain the optical properties of the film

\[ \frac{\Delta R}{R} = \frac{h 4\omega \cos \varphi}{c} \text{Im} \left( \frac{\Delta \varepsilon_S}{\varepsilon_b - 1} \right) = \frac{\Delta \varepsilon_S}{\varepsilon_b - 1} = \frac{\Delta \varepsilon''_S}{\varepsilon_b - 1} \]

For the spectra of changes of imaginary part of the dielectric function of the film \( \Delta \varepsilon''_S \) (CIPDF) to interpret,
FIG. 1: (a) The dependencies of $\Delta R/R$ versus coverage of In film deposited at RT at $E = 1.9$ eV. The vertical lines are the boundaries between linear regions. The solid lines are plotted using least-squares method. (b) The spectra of $\delta \Lambda''_\Theta$ calculated for the 1st, 2nd and 3rd regions. (c) The spectra of $\delta \Lambda''$ calculated for the 1st and 2nd regions. (d) The spectra of $\delta \Lambda''$ (for reference) obtained for elevated-temperature In surface phases: Si(111)7 × 7-In, Si(111)$\sqrt{3} \times \sqrt{3}$ and Si(111)4 × 1. The 1st and 2nd are semiconducting surface phases and the last is metallic one. The position of Si band gap is marked by dashed line.

information about crystallinity and homogeneity of the film obtained by another techniques should be used.

However, the experimental dependence $\Delta R/R(h)$ is not linear in the whole range. It consists of several linear regions that we attribute to the stages of the film growth (Fig. 3(a)). Therefore, we use different standards for calculating the DRC for each region. The number of standards equals to that of linear regions. For each region where the dependence is linear, Eqs. (2) and (3) can be applied. It suffices to use $\Delta R/R^* = \Delta R/R(h) - \Delta R/R(h_i)$ and $h^* = h - h_i$, where $h_i$ is film thickness used as the standard for this region, $\Delta R/R(h_i)$ is DRC for this standard, then the dependence $\Delta R/R^*$ versus $h^*$ is proportional, as in Eq. (2). The described procedure is named the 'method of dynamic standard' (MDS) [3]. Equation (2) is correct for 3D objects (chemical compounds and crystallites of bulk materials); Eq. (3) was used in this work to process the DRC spectra obtained for the reactive system (Cr/Si(111)).

For studying the non-reactive system (In/Si(111)), the equation of Bagchi [5] containing the optical function of 2D objects $\delta \Lambda$ should be used. In order to solve it we inserted a new variable $\delta \Lambda''_\Theta$ named the imaginary part of the normalized variation of the response function (IPNVRF). It is proportional to the slope $K$ of dependence of DRC versus In coverage $\Delta R/R(\Theta)$ (Fig. 1(a)):

$$\delta \Lambda''_\Theta = K_{\epsilon b} \frac{C}{4\omega \cos \phi} (\epsilon_b' - 1).$$  (4)

The meaning of the IPNVRF is the changes of optical properties of a 2D object in the phase transition involving 1 ML of adsorbate (Indium). Using MDS and Eq. (4) for dependence $\Delta R/R(\Theta)$ we found a solution of the Bagchi equation:

$$\delta \Lambda'' = \sum_{i=1}^{N} \delta \Lambda''_{\Theta_i}(\Theta_i - \Theta_{i-1}),$$  (5)

where $\delta \Lambda''$ is the imaginary part of variation of response function (IPVRF), $\Theta_i$ and $\Theta_{i-1}$ are saturation coverage of next and previous surface phase (reconstruction), respectively, $\delta \Lambda''_{\Theta_i}$ is IPNVRF of this phase transition, $N$ is the number of phase transition, and $\Theta_0 = 0$ ML. To calculate the IPVRF, the values $\Theta_i$ can be used either obtained from the dependence $\Delta R/R(\Theta)$ (see below) or from STM data in other papers (if the 1st method does not give accurate values). Although IPVRF and IPVRF have similar symbols and abbreviations, they are different variables. IPVRF is the characteristic of optical properties of 2D objects and its unit is ML. IPNVRF describes
FIG. 2: Empty-state STM images of In/Si(111) interface obtained by RT deposition: (a) 0.08 ML, $U = +1.7$ V; (b) 0.22 ML, $U = +1.0$ V; (c) 0.36 ML, $U = +1.8$ V; (d) 0.55 ML, $U = +1.9$ V; (e) 0.65 ML, $U = +1.8$ V. Scale: $50 \times 50$ nm$^2$. Sample bias voltage denoted by symbol $U$.

FIG. 3: (a) The dependence of $\Delta R/R$ versus thickness of Cr film deposited at RT at $E = 2.11$ eV. The vertical lines are the boundaries between linear regions. The solid lines are plotted using least-squares method. (b) The spectra of $\Delta \varepsilon''$ calculated for all regions.

changes of optical properties during phase transition and has no units. Moreover, the shapes of IPVRF and IPN-VRF spectra are usually different (Figs. 1(b,c)) except those for the 1st phase transition.

III. RESULTS AND DISCUSSION

The dependence of DRC versus In coverage obtained for In/Si(111) system is presented in Fig. 1(a). It con-
tains four linear regions. Because the number of points at each linear region is not enough for the boundary positions to determine precisely in Fig. 1(a), the points of bending (0.12, 0.25 and 0.38 ML) were obtained by averaging the values calculated for dependence $\Delta R/R(\Theta)$ at several photon energies. The regions (0 − 0.12 ML, 0.12 − 0.25 ML, 0.25 − 0.38 ML, and 0.38 − 0.55 ML) correspond to the four stages of In film growth. According to STM data, the 1st and 2nd stages are attributed to MC formation (Figs. 2(a,b)). The 1st type MC consists six In atoms located mainly at faulted half unit cell (FHUC) of Si(111)7×7 [2] (Fig. 2(a)). It appears at the 1st stage (Fig. 2(a)) and its saturation coverage is 0.12 ML [2]. In the 2nd type MC both unfaulted half unit cell (UFHUC) and FHUC of Si(111)7×7 are occupied by In atoms (six per each half) (Fig. 2(b)). These MC cover Si surface at the 2nd stage; its saturation coverage is 0.24 ML [2]. The positions of the 1st and 2nd bending points (0.12 and 0.25 ML) are close to the saturation coverage for MC formed at the 1st and 2nd stages (0.12 and 0.24 ML) (Fig. 1(a)). Therefore, for saturation coverage of the studied surface structures to obtain, bending points should be found in the dependence $\Delta R/R(\Theta)$. This statement is the basis of the new method we propose for obtaining the saturation coverage.

Applying this method, we suggested that 3rd bending point (0.38 ML) is close to the saturation coverage of clusters growing at the 3rd stage (Fig. 2(c)). This value corresponds to 18 In atoms per a unit cell of Si(111)7×7 or nine In atoms per a half unit cell because of symmetric filling of both half unit cells (Fig. 2(c)). Therefore, the 3rd type cluster contains 18 atoms per a unit cell and its saturation coverage is 0.38 ML. At the last (4th) stage the next layer of In atoms grows atop the 3rd type clusters (Fig. 2(d)). Unfortunately, the dependence $\Delta R/R(\Theta)$ does not contain the 4th bending point; we used STM data (Fig. 2(d)) and the saturation coverage for the 3rd type cluster to find that for the 4th type clusters. We calculated that the saturation coverage of the 4th type clusters is close to 0.65 ML. In order to verify the obtained value we deposited 0.65 ML of IN onto Si(111)7×7 at RT (Fig. 2(e)). One can see the surface is completely covered by the 4th type clusters (compare Fig. 2(d) and Fig. 2(e)).

Optical spectra of the studied MC are presented in Figs. 1(b,c). IPVRF spectrum for the 3rd type clusters is not shown in Fig. 1(c) because the saturation coverage for them (0.38 ML) required for IPVRF calculation (see Eq. (5)) should be found accurately before using it. IPNVRF spectra are shown in Fig. 1(b). They describe changes of optical properties during phase transition (number ‘i’ phase → number ‘‘i’’ phase) and are related with their band structures:

$$\delta A^\nu_{\Theta}$$

$$= \frac{4\pi^2e^2}{m^2\omega^2A(\Theta - \Theta_{i-1})} \times \sum_{v,c} \left| \mathbf{p}_{v,c}(\mathbf{k}_i) \right|^2 \delta (E_C(\mathbf{k}_i) - E_v(\mathbf{k}_i) - \hbar\omega)$$

$$- \sum_{\mathbf{k}_i-1} \left| \mathbf{p}_{v,c}(\mathbf{k}_i-1) \right|^2 \delta (E_C(\mathbf{k}_i-1) - E_v(\mathbf{k}_i-1) - \hbar\omega),$$

where $\mathbf{p}_{v,c}(\mathbf{k}_i)$ and $\mathbf{p}_{v,c}(\mathbf{k}_i-1)$ are the momentum operators (contains density of state (DOS)) between initial (v) and final (c) slab states at the point in 2D Brillouin zone.
continuous film. CIPDF spectrum of this film is smooth (Fig. 3(b)). The peak positions do not coincide with those of both well-known Cr silicides and bulk Cr crystallites [7]. It suggests the film consists of two substances at least.

Unlike the spectrum of a continuous film, the CIPDF of quasi MC contain sharp peaks (Fig. 3(b)). Positions of peaks are not changed and they are close to those of CrSi ones [7]. Therefore growth of 2D and 3D CrSi crystallites was suggested at the 1st and 2nd stages, respectively.

The CrSi crystallites growth in FHUC implies that atomic structure of top layers of FHUC of 7 × 7 surface phase, namely the 2nd and 3rd ones, is more suitable for CrSi formation than that of UFHUC. Decreasing and broadening of peaks height observed in the 2nd spectrum results from non-regular increasing of CrSi island sizes. The double increasing of Cr deposition rate results in considerable peaks broadening and the shape of the 2nd spectrum becomes metallic-type up to 2.3 eV, i.e. \( \Delta E_E \sim (E) - a \), where \( a > 0 \) (spectrum III in Fig. 7(b) in [3]). It suggests noticeable increasing of CrSi crystallite size variation. The 1st stage of Cr film growth is also changed: formation of CrSi\textsubscript{2}-like compound occurs. However, CIPDF of the last stage (spectrum IV in Fig. 7(b) in [3]) is close to that of the 3rd one in Fig. 3(b). It means that double increasing of Cr deposition rate does not influence noticeably the film growth at the last stage [6]. Therefore, at the 3rd stage, formation of both CrSi crystallites and CrSi\textsubscript{2}-like compound between them occurs.

Finally, the difference in optical properties between reactive and non-reactive clusters should be noticed. The spectra of reactive (Cr) clusters are positive (Fig. 3(b)) while those of non-reactive (In) ones contain negative values (Fig. 1(c)).

IV. CONCLUSIONS

Using differential reflectance spectroscopy, optical functions of Indium MC and Chromium quasi MC were obtained. We found that during formation of clusters the positions of peaks in spectra of optical function of Cr quasi MC do not change. It suggests that Cr clusters keep their composition during growth. Having analyzed the obtained spectra, we conclude that Cr quasi MCs are 2D (when Cr film thickness is lower than 0.03 nm) and CrSi crystallites are 3D. Indium MC form surface phases. The Si surface covered by the 1st type In MC is a metallic surface phase while that consisting of the 2nd type In MC is semiconducting one.

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