Calculation of Desorption Parameters for Mg/Si(111) System*

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The method for calculation of desorption parameters developed for differential reflection spectroscopy is presented. It enables to study desorption and to control phase composition of film simultaneously. Spectra of differential reflectance \( \Delta R/R \) of the film are initial data for the method. The method was used for Mg/Si(111) system. The desorption parameters for bulk Mg film were calculated and limitations of the method were found.

Keywords: Metallic films; Thermal desorption; Alkaline earth metals; Silicon; Reflection spectroscopy; Magnesium; Desorption parameters; Si(111)

I. INTRODUCTION

The system of Mg/Si(111) attracts attention of scientists because of narrow-gap semiconductor silicide (Mg2Si) formation. The silicide islands grow epitaxially on Si(111) and specific thermoelectromotive of this material embedded in Si substrate is high [1]. However low value of the Mg desorption temperature influences appreciably on Mg adsorption rate. It complicates exact calculation of deposited film thickness, comparing obtained data with previous ones and building the model of Mg film growth. Therefore calculation of desorption parameters of Mg in the Mg/Si(111) system \((v_0; \text{ maximum desorption rate}, E_{\text{des}}; \text{ activation energy of desorption})\) is primary task. However phase composition of deposited Mg film depends on the Mg adsorption rate. Therefore new method for calculation of desorption parameters enabling to study desorption and to control phase transition of Mg film simultaneously should be developed to solve this task. The developing of this method and use it for the Mg/Si(111) system were aims of our paper.

II. EXPERIMENTAL

The experiments were carried out in ultrahigh vacuum (UHV) chamber “Varian” with base pressure \(1.5 \times 10^{-8} \text{ Pa}\), which was equipped with Auger electron spectroscopy (AES), electron energy loss spectroscopy (EELS) and differential reflection spectroscopy (DRS) techniques. The samples \((15 \times 6 \times 0.38 \text{ mm})\) were cut from \(n\)-type Si wafer \((0.3 \Omega-\text{cm})\). Surface phase of clean Si(111) surface (phase \((7 \times 7))\) was prepared by several flash heating at \(1250^\circ \text{C}\) in UHV chamber. Initial state of sample was continuous bulk Mg film grown on continuous buffer Mg2Si layer covering surface Si(111). It was grown by Mg deposition on clean surface Si(111) for 10 minutes at different temperatures \((100-220^\circ \text{C})\). This temperature range was chosen because the Mg desorption rate in this range is appropriate for it to find by developed method. Study of Mg desorption included 2 stages. At 1st stage Mg deposited on initial sample for 5 minutes at certain temperature to grow bulk Mg film being desorbed for 5 minutes at the same temperature at 2nd stage. Formation of initial sample and study of Mg desorption were realized at similar growth condition and at constant substrate temperature and the rate of Mg atoms deposition. Magnesium was evaporated from tantalum tube. To reduce sample heating by evaporation unit the distance between unit and sample was \(8 \text{ cm}\). The rate of Mg atoms deposition \(v_{\text{dep}}\) \((v_{\text{dep}} = 0.6 \text{ nm/min})\) was calibrated by quartz sensor at room temperature (RT). EELS spectra were used to study uniformity and composition of Mg film for initial sample and for bulk Mg film desorbed at certain temperature. Only samples covered by continuous bulk Mg film both before Mg deposition and after Mg desorption were used for study of Mg desorption. DRS spectra were recorded in photon energy range \(1.13-2.5 \text{ eV}\) during Mg deposition on initial sample at constant temperature. Detailed description of DRS technique is presented in Ref. [2].

III. RESULTS AND DISCUSSIONS

A. Method for calculation of desorption parameters

The new method for calculation of desorption parameters will be developed for DRS. The value obtained by DRS technique is differential reflectance:

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

where \(R_0\) and \(R(\Delta h)\) are reflectance for initial sample and for the same sample covered by thickness \(\Delta h\) deposited film of adsorbate, respectively. Thickness of film grown at temperature \(T\) is \(\Delta h = (v_{\text{dep}} - v_{\text{des}}(T))\Delta t\), where \(\Delta t\) is deposition time, \(v_{\text{dep}}\) and \(v_{\text{des}}(T)\) are the rates of atoms deposition at RT and desorption at temperature \(T\), respectively. To find relation(s) for value \(\Delta R/R\) and optical functions of phases the grown film consists of, the following is to be carried out: 1) to build a model of the film growth, 2) to use the model for finding \(\Delta R/R(\Delta t, \omega)\) function, where \(\omega\) is light frequency, 3) to separate variables in \(\Delta R/R(\Delta t, \omega)\) function by combining frequency dependent variables and constants in \(K(\omega)\) function(s) (These functions contain optical functions, which describe optical properties of phases the grown film consists of.), 4) to find...
The equation (3) should be solved using Kramers-Kronig’s formulas which are relations for real and imaginary parts of dielectric function [5]. If the highest photon energy applied in investigations is lower than energy of photon the first direct transition produces in substrate (phase B), $D(\omega) = 1/(1 + \Delta R_0/R)$ is corrective function, $\varepsilon_A = \varepsilon'_A + i\varepsilon''_A$ is dielectric function of adsorbate (phase A) and $K_{ad}(\omega, T)$ is slope of linear region of dependence $\Delta R/R$ on deposition time $\Delta t$ for deposition stage:

$$K_{ad}(\omega, T) = \frac{4\omega D(\omega) \cos \varphi (v_{dep} - v_{des}(T))}{c} \cdot \text{Im} \left( \frac{\varepsilon_A(\omega) - 1}{\varepsilon_B(\omega) - 1} \right).$$

The dielectric function of film $\varepsilon$ describes optical properties of bulk phase. Spectrum of imaginary part of dielectric function of film $\varepsilon''$ calculated by use of formulas (4) and (5) is used for investigated phase identification. Value $\varepsilon''$ is decreased for metallic phases, and when light frequency $\omega$ is increased, the dependence of $\varepsilon''$ versus $\omega$ is $\varepsilon'' \sim \omega^{-a}$, where $a$ is constant [5]. Appreciable peaks at spectrum $\varepsilon''$ are distinguishing characteristic of semiconductor phases. Comparing these peaks positions and values obtained for the potential phases, the investigated phase can be identified exactly. Therefore this method of calculation of desorption parameters enables to study desorption and to control phase transition of film simultaneously.

B. Calculation of desorption parameters for Mg in Mg/Si(111) system

Curves $\Delta R/R(\Delta t)$ obtained for Mg deposition (region 1) and desorption (region 2) in the Mg/Si(111) system at different temperatures are presented in Fig. 1. Dependence $\Delta R/R$ on deposition (desorption) time $\Delta t$ is linear and so it correlates with formula (2). The value of slope of curve $\Delta R/R(\Delta t)$ for deposition is positive and that for desorption is negative, as it was predicted by formulas (4) and (5). The shape of $\varepsilon'_A$ spectra obtained for deposition and desorption corresponds to bulk Mg film. Formation of bulk Mg film is also conformed by EELS spectra. To find region of correctness of calculated desorption rate $v_{des}$, dependence of the rate on photon energy at 170°C is presented in Fig. 2. The shape of this dependence is not greatly changed at different temperatures and so these curves are not shown in Fig. 2. According to Fig. 2, photon energy range 1.13-1.75 eV is the region of correctness of calculated desorption rate. For Eq. (8) to formulate, $v_{des}(T)$ values were used from this region. The calculated desorption parameters for bulk Mg film are: $v_0=17630026$
FIG. 1: Curves of $\Delta R/R(\Delta t)$ obtained at different temperatures for Mg film growth (region 1) and desorption (region 2) in Mg/Si(111) system at photon energy 1.13 eV. Solid lines are linear fitting of experimental data.

FIG. 2: (I) Desorption rate of Mg film at 170°C and (II) activation energy of desorption $E_{\text{des}}$ obtained in the range used. $V_{\text{des}} = 0.733 \pm 0.001$ nm/min, $E_{\text{des}} = 0.733 \pm 0.001$ eV. The maximum temperature of bulk Mg film formation obtained during experiments for $v_{\text{dep}} = 0.6$ nm/min (215°C) is close to the value obtained during experiments (219.8°C). It is close to the value obtained during experiments (215°C).

IV. CONCLUSIONS

The method of calculation of desorption parameters developed in this article enables to study desorption and to control phase transition of film simultaneously. It results from involving capability of differential reflection spectroscopy in this method. Growth of continuous bulk film and desorption from this film result in linear dependence $\Delta R/R$ on deposition (desorption) time $\Delta t$. To calculate desorption rate at certain temperature, only deposition rate and values of slope of curves $\Delta R/R(\Delta t)$ obtained for deposition and desorption at the same temperature are used.

The method of calculation of desorption parameters was used for Mg film in the Mg/Si(111) system. Fine correlation of theoretical formulas and experimental $\Delta R/R(\Delta t)$ curves was observed. The obtained desorption parameters for bulk Mg film enable to calculate the maximum temperature of bulk Mg film formation for $v_{\text{dep}} = 0.6$ nm/min (219.8°C). It is close to the value obtained during experiments (215°C).

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Appendix

The used model of film growth meets following requirements (Fig. 3):

1. Initial sample located in vacuum consists of bulk phase A film, buffer phase $A_xB_y$ layer, semi-infinite substrate of bulk phase B, interface layers $i_B$ and $i_A$ and surface phase $s_A$ (II). Plane $XOY$ coincides with this interface layer $i_B$. Value $z$ is increased, when one moves from vacuum to substrate.

2. The phase A film and buffer phase $A_xB_y$ layer are continuous during film growth (III).

3. Shape of islands of phase $A_xB_y$ is rectangular parallelepiped. Another shape of islands is also accepted. However the final formula (6) does not depend on island shape, because this characteristic of island disappears in averaging formula (18).

4. At the interface phase of $A$–vacuum ($z = -d_{AxB_y}$ and $z = -d_{AxB_y} - d_i - \Delta d_i$ for $i$ island before atoms $A$ deposition (I) and after $\Delta t$ minutes deposition (III), respectively) formation of surface phase $s_A$ occurs.

5. Interfaces of phase $A_xB_y$–phase B ($z=0$) and phase $A$–phase $A_xB_y$ ($z = -d_{AxB_y}$) are interface layers $i_B$ and $i_A$, respectively.

6. Thickness of buffer phase $A_xB_y$ layer is not changed during film growth, i.e. phase $A$ atoms are not desorbed from phase $A_xB_y$, and do not react with phase B to produce additional molecules of phase $A_xB_y$.

7. Boundaries of phases are abrupt.

The used model of film growth meets following requirements (Fig. 3):

1. Initial sample located in vacuum consists of bulk phase A film, buffer phase $A_xB_y$ layer, semi-infinite substrate of bulk phase B, interface layers $i_B$ and $i_A$ and surface phase $s_A$ (II). Plane $XOY$ coincides with this interface layer $i_B$. Value $z$ is increased, when one moves from vacuum to substrate.

2. The phase A film and buffer phase $A_xB_y$ layer are continuous during film growth (III).

3. Shape of islands of phase $A_xB_y$ is rectangular parallelepiped. Another shape of islands is also accepted. However the final formula (6) does not depend on island shape, because this characteristic of island disappears in averaging formula (18).

4. At the interface phase of $A$–vacuum ($z = -d_{AxB_y}$ and $z = -d_{AxB_y} - d_i - \Delta d_i$ for $i$ island before atoms $A$ deposition (I) and after $\Delta t$ minutes deposition (III), respectively) formation of surface phase $s_A$ occurs.

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6. Thickness of buffer phase $A_xB_y$ layer is not changed during film growth, i.e. phase $A$ atoms are not desorbed from phase $A_xB_y$, and do not react with phase B to produce additional molecules of phase $A_xB_y$.

7. Boundaries of phases are abrupt.
where \( c = 3 \times 10^8 \) metres per second is fundamental constant named the rate of light in vacuum, \( \varphi \) is angle of light beam incidence, \( \varepsilon_B = \varepsilon_B' + i\varepsilon_B'' \) is dielectric function of substrate (phase B), \( \omega \) is light frequency. Differential reflectance calculated in Bagchi’s approach equals

\[
\frac{\Delta R'}{R} = \frac{R(\Delta h) - R_{sB}}{R_{sB}},
\]

where \( R_{sB} \) is reflectance for semi-infinite phase B substrate covered by surface phase \( sB \) (I in Fig. 3). It differs from experimental value of differential reflectance \( \Delta R/R \) calculated by use of formula (1). Therefore to apply formula (10) for our experimental condition, interrelation of experimental value \( \Delta R/R \) and theoretical one \( \Delta R'/R \) should be found. Having divided numerator and denominator of experimental value \( \Delta R/R \) and theoretical one \( \Delta R'/R \) in it, we obtained this dependence:

\[
\frac{\Delta R}{R} = \frac{\Delta R(\Delta h)/R - \Delta R_0/R}{\Delta R_0/R + 1} = D(\omega) \left( \frac{\Delta R(\Delta h)/R - \Delta R_0/R}{\Delta R_0/R} \right),
\]

where \( D(\omega) = 1/(1 + \Delta R_0/R) \) is corrective function, \( \Delta R_0/R \) and \( \Delta R(\Delta h)/R \) are differential reflectance calculated in Bagchi’s approach for initial sample and for the same sample covered by thickness \( \Delta h \) deposited film of adsorbate, respectively. The appearance of corrective function \( D(\omega) \) in formula (12) means that formula (10) should be multiplied by \( D(\omega) \) to conform to our experimental condition.

Spectrum of variation of response function \( \delta \lambda(\omega) \) presented in formula (10) consists of other structures contribution to optical properties of film, namely contribution of bulk phases A and \( A_xB_y \), surface phase sA and interface layers iB and iA. Within the framework of Bagchi’s approach [3] we derived relation for optical function of these structures and spectrum \( \delta \lambda(\omega) \):

\[
\delta \lambda = \frac{1}{S_0} \sum_{i=1}^{N} S_i \int_{-\infty}^{\infty} (\langle \varepsilon_i^{(a)}(z) \rangle - \langle \varepsilon_i(z) \rangle) dz,
\]

where \( S_0 \) is area of light beam used for sample investigation, \( S_i \) is area of top surface of \( i \) island of phase A. 

8. Thickness of surface phases and interface layer is zero. However a value of optical functions of these 2D structures is finite.

9. Deposited film of adsorbate is thin.

The 3rd, 7th and 8th items of this model enable to use Bagchi’s approach [3] for deriving basic formula for continuous film:

\[
\frac{\Delta R'}{R} = \frac{4\omega \cos \varphi}{c} \text{Im} \left( \frac{\delta \lambda(\omega)}{\varepsilon_B(\omega) - 1} \right),
\]

FIG. 3: Model of film growth, where I is semi-infinite substrate, II is initial sample, and III is initial sample subjected deposition of thickness \( \Delta h \) film of adsorbate A. sB and sA are surface phases of substrate medium (phase B) and adsorbate (phase A), respectively. iB and iA are interface layers. \( S_i \) and \( d_i \) are area and height of \( i \) island of phase A, respectively.
\[
\langle \varepsilon_i^{(a)}(z) \rangle = \begin{cases} 
\delta \Lambda_{A_{d}B_{y}} \delta (z + d_{A_{x}B_{y}} + d_i), & \varepsilon_A, \\
\delta \Lambda_{A_{d}B_{y}} \delta (z + d_{A_{x}B_{y}}), & \varepsilon_{A_{x}B_{y}}, \\
\delta \Lambda_{A_{d}B_{y}} \delta (z), & \varepsilon_{B_{y}}, \\
0, & (0; \infty)
\end{cases}
\]

or

\[
\langle \varepsilon_i^{(a)}(z) \rangle = \begin{cases} 
\delta \Lambda_{A_{d}B_{y}} \delta (z + d_{A_{x}B_{y}} + d_i), & \varepsilon_A, \\
\delta \Lambda_{A_{d}B_{y}} \delta (z + d_{A_{x}B_{y}}), & \varepsilon_{A_{x}B_{y}}, \\
\delta \Lambda_{A_{d}B_{y}} \delta (z), & \varepsilon_{B_{y}}, \\
0, & (0; \infty)
\end{cases}
\]

To satisfy the item 8 of model, optical functions of 2D structures were multiplied by delta-function \( \delta (z) \). Substituting the values of dielectric functions in the formula (13) produces:

\[
\delta \Lambda_0 = \frac{1}{S_0} \sum_{i=1}^{N} S_i [d_i (\varepsilon_A - 1) + d_{A_{x}B_{y}} (\varepsilon_{A_{x}B_{y}} - 1) + \delta \Lambda_{A_d} + \delta \Lambda_{A_i} + \delta \Lambda_{B_d} - \delta \Lambda_{B_i}], \\
\delta \Lambda(\Delta h) = \frac{1}{S_0} \sum_{i=1}^{N} S_i [(d_i + \Delta d_i) (\varepsilon_A - 1) + d_{A_{x}B_{y}} (\varepsilon_{A_{x}B_{y}} - 1) + \delta \Lambda_{A_d} + \delta \Lambda_{A_i} + \delta \Lambda_{B_d} - \delta \Lambda_{B_i}],
\]

where \( \delta \Lambda_0 \) and \( \delta \Lambda(\Delta h) \) are variation of response function for initial sample and for the same sample covered by thickness \( \Delta h \) deposited film of adsorbate, respectively. Having substituted in the formula (10), the formulas (14) and (15) produce \( \Delta R_0^R/R \) and \( \Delta R(\Delta h)^R/R \), respectively. Direct substitution of \( \Delta R_0^R/R \) and \( \Delta R(\Delta h)^R/R \) in the formula (12) yields the relation for \( \Delta R/R \) and optical functions of phases the film consists of:

\[
\frac{\Delta R}{R} = \frac{4 \omega D(\omega) \cos \varphi}{c S_0} \text{Im} \left( \frac{\varepsilon_A(\omega) - 1}{\varepsilon_B(\omega) - 1} \right) \sum_{i=1}^{N} S_i \Delta d_i. 
\]

Direct substitution of the expressions (17) and (18) in the formula (16) yields:

\[
\frac{\Delta R}{R} = \frac{4 \omega D(\omega) \cos \varphi (v_{\text{dep}} - v_{\text{des}}(T))}{c} \text{Im} \left( \frac{\varepsilon_A(\omega) - 1}{\varepsilon_B(\omega) - 1} \right) \Delta t.
\]

where \( v_{\text{dep}} \) and \( v_{\text{des}}(T) \) are the rates of phase A atoms deposition at RT and desorption at temperature \( T \), respectively. Effective height of this island is related to the values \( S_i \) and \( \Delta d_i \) for islands of phase A:

\[
\Delta d = \Delta h = (v_{\text{dep}} - v_{\text{des}}(T)) \Delta t, \\
\Delta h = \sum_{i=1}^{N} S_i \Delta d_i / S_0.
\]

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