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Non-constant diffusion characteristics of nanoscopic Mo–Si interlayer growth

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ABSTRACT

In situ small-angle X-ray reflection and wide angle X-ray diffraction of synthetic, Mo–Si based multilayer structures were used to study layer interdiffusion dynamics at temperatures between 250 and 300 °C. The in situ reflection measurements revealed information on non-constant interdiffusion characteristics during the interlayer growth. The activation energy for interdiffusion was found to gradually increase with growing Si-on-Mo interlayer thickness, towards a saturation level of approximately 2.5 eV. Contrary, the activation energy for interdiffusion at the Mo-on-Si interlayer was almost constant at a value around 2.6 eV. Wide angle X-ray diffraction at different stages in the annealing cycle further showed the evolution of Mo crystallites. Evolution of these crystallites was found to be strongly correlated to the change in period thickness of the multilayer structures.

1. Introduction

Several studies have reported on silicide formation as a result of Mo–Si interdiffusion with the value of the activation energies for interdiffusion ranging from 0.5 to 2.4 eV [1–6]. Especially the difference in results from Bruijn et al. [5] (0.5 eV), Nakajima et al. [3] (1.1 eV) and Rosen et al. [4] (2.4 eV) is remarkable, given the similarity of the experimental conditions, like bilayer thickness of the Mo/Si multilayer structure and annealing temperatures.

It has been reported that the diffusion rate in Mo/Si multilayer structures, having a bilayer thickness of only 0.8 nm, is time dependent [2]. The authors attributed this time dependence to structural relaxations. However, using high resolution electron microscopy, Rosen et al. observed a rapid initial growth of the Mo–Si interlayers, before the interlayer grew parabolically in time. Therefore, structural relaxation cannot explain the anomalous growth in the thicker multilayer structures.

To resolve the above discrepancies in the observed values of the activation energies, and to be able to follow the diffusion dynamics during all stages of the interlayer growth, analysis with an improved spatial resolution is required. In this paper, we study the diffusion dynamics at a picometer scale for the Si-on-Mo and Mo-on-Si interlayers. We use in situ small angle X-ray reflection during annealing in the temperature range of 250–300 °C to monitor changes in the period thickness, especially during the rapid initial interlayer growth.

2. Experimental details

Multilayer structures consisting of 50 periods were deposited on Si (100) substrates by DC magnetron sputtering in a chamber with a base pressure lower than 1e−6 Pa. The periodical structures of the multilayer systems are given by [B_4C (1.5 nm)/Mo (3 nm)/Si (4 nm)] and [Mo (3 nm)/B_4C (1.5 nm)/Si (4 nm)]. The relatively thick B_4C layer at one of the two interfaces significantly reduces interdiffusion, even up to 400 °C [7], so that any total multilayer phenomenon, like period thickness change, can easily be ascribed to a (diffusion) process at the opposite interface. The evolution of the period thickness of the multilayer structures during annealing was studied using hard-ray reflectometry. Some specific details of the diffractometer are: Cu-Kα (0.154 nm) radiation, four bounce asymmetrically cut Ge (220) monochromator, and instrumental broadening of 0.005°.

The method we use to monitor the periodical thickness of multilayer structures during annealing using hard X-ray reflectometry has been discussed by Bruijn et al. [5]. For convenience we will summarize the most important parts here.

The periodical structure of a Bragg mirror consists of two or more layers of different optical materials. For certain angles θ, waves reflected at the interfaces interfere constructively. The n*th* Bragg angle for constructive interference is given by the corrected Bragg equation

$$n\lambda = 2\Lambda \sin\theta_n \sqrt{1-\frac{2\bar{\delta}}{\sin^2\theta_n}}, \quad (1)$$

where λ is the wavelength of the radiation, Λ is the thickness of the period, and $\bar{\delta}$ is the average refractive index decrement. During

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annealing, it is required that the change in period thickness is measured with a high time resolution. Therefore, only a limited number of Bragg peaks are measured to reduce the measurement time of a single scan. To improve accuracy and remove possible misalignment in θ of the sample in the Bragg–Brentano setup, we derive an equation to determine the change in period thickness from the change in relative distance between two Bragg orders at two consecutive times. First we subtract the position of two Bragg orders at time t_j

$$\frac{(m-n)\lambda}{2\Lambda(t_j)} = \sin\theta_m(t_j)\left(1-\frac{\bar{\delta}}{\sin^2\theta_m(t_j)}\right) - \sin\theta_n(t_j)\left(1-\frac{\bar{\delta}}{\sin^2\theta_n(t_j)}\right) \approx \theta_m(t_j) - \theta_n(t_j). \tag{2}$$

The approximation is valid for small angles and $\bar{\delta} \ll \theta$, which is usually satisfied for hard X-rays. After subtracting the previous equation for two different times we obtain

$$\Lambda(t_2) = \frac{(m-n)\lambda\Lambda(t_1)}{(m-n)\lambda + 2(\Delta\theta_m - \Delta\theta_n)\Lambda(t_1)}, \tag{3}$$

where $\Delta\theta_i$ is the shift in Bragg angle between times t_1 and t_2 for Bragg order $i=(m,n)$. During annealing we measured two pairs of Bragg angles, for example orders $(m,n)=(2,7)$ and $(m,n)=(2,8)$ and averaged over the results. With a total scan range of 1.3° with steps of 0.005° and a count time of 1 s per angle, the scan time of the three Bragg peaks is 260 s. This time is the time resolution of our method to determine the change in period thickness. The error in change of period thickness is approximately 1 pm.

In a Bragg mirror consisting of two materials, interdiffusion occurs at the two different interfaces, namely A-on-B and B-on-A. The interdiffusion effects at both interfaces/interlayers can be different. For example, Erdélyi et al. [8] showed that the diffusion coefficient can depend quite strongly on local composition. Consequently, the change in period thickness is related to the amount and stoichiometry of interlayer formed upon interdiffusion at both interfaces. The change in period thickness is given by

$$\Delta\Lambda(t) = [x_{A-B}(t) - x_{A-B}(t=0)]\Delta z_{A-B} + [x_{B-A}(t) - x_{B-A}(t=0)]\Delta z_{B-A}, \tag{4}$$

where $x(t=0)$ is the initial width of the silicide interlayer formed after deposition of the multilayer structures, $x(t)$ is the total interlayer width at time t, and Δz is a dimensionless thickness change parameter due to interdiffusion of A and B. The labels *A–B* and *B–A* refer to the A-on-B or the B-on-A interface, respectively. In this study, the *B–A* term in Eq. (4) is removed by introducing B_4C at this particular interface, where *A–B* is then the alternating interface, without barrier, either Mo-on-Si or Si-on-Mo.

For the calculation of a change in period thickness, we still have to provide a value for the thickness change parameter. For this we consider the following reaction: *x mole of A + y mole of B → 1 mole of* A_xB_y. Transforming this to molar volumes using bulk density values and neglecting strain effects, we get an estimation for $\Delta z_{A_xB_y}$ by taking the cube root of the normalized change in volume.

From the measurements, the change in period thickness is given by

$$\Delta\Lambda(t) = \Lambda(t) - \Lambda_0 - \Delta\Lambda_T, \tag{5}$$

where Λ_0 is the initial period thickness at room temperature, $\Lambda(t)$ using Eq. (3) is the period thickness at time t at the annealing temperature T, and $\Delta\Lambda_T$ is the thermal expansion of a single period. The thermal expansion was estimated from the difference between the derived period thickness at the end of the annealing cycle at temperature T and the period thickness derived after cooling the structure down to room temperature. The added interlayer thickness during the interdiffusion process is very small compared to the total period thickness, therefore the difference in thermal expansion of the structure during annealing can be neglected.

Apart from a rapid initial interlayer growth [4], Mo–Si interlayer growth is reported to be diffusion limited [1,3–5]. In this case, a parabolic relation exists between the interlayer width and the diffusion rate D,

$$x^2 \propto Dt. \tag{6}$$

From Eq. (4) under the simplified condition that we can neglect period contraction effects at one interface type, we obtain for the interlayer width squared

$$x^2(t) = \frac{1}{\Delta z_{A-B}^2}\left(\Delta\Lambda^2(t) + x_0^2\Delta z_{A-B}^2 + 2\Delta\Lambda(t)x_0\Delta z_{A-B}\right), \tag{7}$$

where $x(t)$ and $x_0(=x(t=0))$ both refer to the A-on-B interlayer.

In addition to measurement of the change in period thickness, we determined the change in size of the Mo crystallites using wide angle X-ray diffraction after several times of annealing at a few selected temperatures. To suppress the diffraction peak of the monocrystalline Si substrate, the sample was rotated by $\phi=20°$. To maximize the illuminated area, the sample was positioned at an angle of $\theta=1°$ with respect to the incident beam.

3. Results and discussion

We subjected the B_4C/Mo/Si and Mo/B_4C/Si multilayer structures to temperature treatments between 250 and 300 °C. The resulting change in the period thicknesses of the B_4C/Mo/Si structures are illustrated in Fig. 1.

Using Eq. (7) we made a first approximation of the interlayer growth by transforming the change in period thickness data to an interlayer width as a function of time, illustrated in Fig. 2. In the calculation we used $x_0=0.5$ nm, a value corresponding to interlayer widths given in literature for the Si-on-Mo interlayer [4,9]. For Δz we used a value corresponding to $MoSi_2$ formation from bulk Mo and Si. This particular compound was chosen, since for Mo–Si interdiffusion at temperatures below 800 °C, (h-)$MoSi_2$ formation is usually reported as the phase of the growing layer [1,6]. The h-$MoSi_2$ phase has the lowest heat of formation of Mo-silicide compounds [10]. The influence of the assumed parameter values on the results will be discussed later.

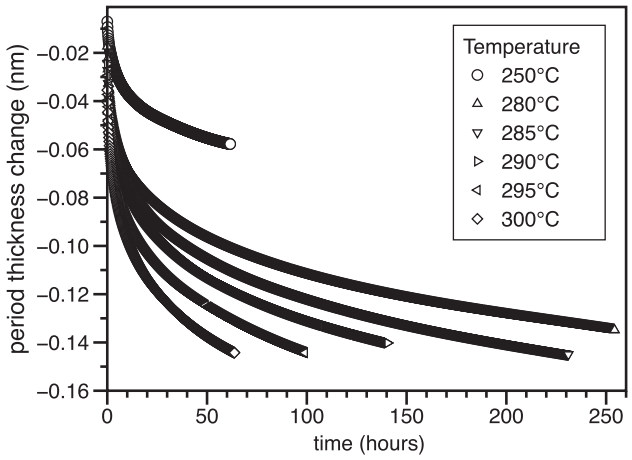

Fig. 1. Period thickness change evolution of the B_4C/Mo/Si structure at annealing temperatures of 250–300 °C.