

Features of diffusion mixing in Mo/Si multilayers

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X-ray photoelectron spectroscopy, transmission electron microscopy, and low-angle X-ray diffraction were used to investigate the diffusion intermixing in multilayer periodic Mo/Si coatings during manufacturing and heating at 340–380°C. It is shown that the mixed zones in the initial state consist of MoSi₂ silicide. Character of mixed zones growth depends on the interface type (Si on Mo or Mo on Si). At initial stage of annealing, the activation energy of interdiffusion has been found to vary from 0.1 to 2.1 eV and from 0.7 to 2.1 eV for the 1-st and 2-nd interface type, respectively.

С помощью рентгеновской фотоэлектронной спектроскопии, просвечивающей электронной микроскопии и малоугловой рентгеновской дифрактометрии исследовалось диффузионное перемешивание в многослойных периодических покрытиях Mo/Si при изготовлении и при нагреве до 340–380°C. Показано, что в исходном состоянии перемешанные зоны состоят из силицида молибдена MoSi₂. Наблюдается различный характер роста перемешанных зон в зависимости от типа границы раздела (Si на Mo или Mo на Si). Установлено, что энергия активации диффузии на начальной стадии отжига изменяется от 0.1 до 2.1 эВ для границы первого типа и от 0.7 до 2.1 эВ – для второго типа.

Mo/Si multilayer coatings are used widely in science and engineering as X-ray optics elements. That is why the multilayer structure was studied at many laboratories [1, 2]. But in spite of the significant progress in understanding of important particularities of Mo/Si multilayer, some features of the system remain still unexplained. For instance, there are no reliable data on chemical composition of the amorphous mixed zones in the as-deposited state. To date, there are no direct structure researches of the mixed zones. Features of diffusion mixing in the system have not been explained. For example, it has been shown [3] that the mixed zones grow at various speeds during annealing, but this observation is not explained yet. In this work, we report data on the mixed zone chemical composition obtained using X-ray photoelectron spectroscopy (XPS). Also we attempt to explain features of diffusion mixing in this system at initial stages.

The multilayer coating of 10.5 nm period was obtained by DC magnetron sputtering. The multilayer structure was studied by transition electron microscopy of the cross-sections (TEM) and low angle X-ray diffraction (LAXRD) with computer simulation of diffraction curves, as described in detail elsewhere [4]. The chemical composition was investigated by X-ray photoelectron spectroscopy with depth profiling using a Perkin-Elmer PHI 6900 instrument using a monochromatic Al K α source with photon energy of 1486.6 eV. The photoelectron energy was analyzed by a hemispherical analyzer with 23.5 eV energy threshold and 0.025 eV energy resolution. The Mo 3d_{5/2} line was studied. We did not study Si_{2s} line because the satellite in the Si_{2s} doublet is difficult to separate. For depth profiling analysis, the ion etching was performed using 1 keV Ar⁺-ion beam at 75° incidence angle. The mathematical data processing

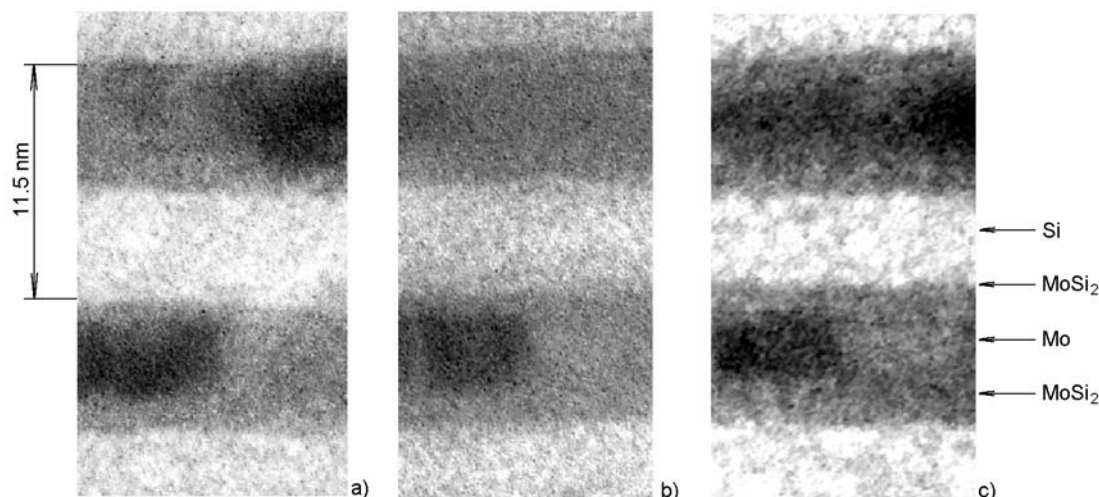


Fig. 1. TEM image of as-deposited Mo/Si multilayer (a) and after annealing at 330°C during 30 min (b) and 30 h (c).

Table 1. Binding energies of Mo_{3d} and Si_{2p} lines measured for references

	Mo	MoSi_2	
	$\text{Mo } 3d_{5/2}$	$\text{Mo } 3d_{5/2}$	$\text{Si } 2s$
Binding energy, eV	227.60	227.25	99.6

was performed using standard procedures from the PHI MATLAB 6 software [5]. For calibration of XPS spectrometer, several references were used, namely, bulk Mo, Si, and 5 μm stoichiometric MoSi_2 film. The measured binding energies for the references are shown in Table 1. The measured shift of $\text{Mo } 3d_{5/2}$ binding energy between pure molybdenum and in silicide is seen to be of 0.2 eV. This value is close to the data from [6].

The TEM image of as-prepared Mo/Si multilayer is shown in Fig. 1a. The coating consists of *c*-Mo and *a*-Si layers. There are amorphous mixed zones between pure Mo and Si. These zones formed during deposition are asymmetrical. When Mo is deposited onto Si (Mo-on-Si interface), the mixed zone is 0.95 nm thick. In case of silicon deposition onto molybdenum (Si-on-Mo interface), the mixed zone thickness is 0.45 nm. The thickness and density of layers obtained from TEM and LAXRD are presented in Table 2. On XPS depth profile, oscillations of signal intensity are seen (Fig. 2). These oscillations correspond to periodical structure of the multilayer coating. The profile tailing is due to the large escape depth for photoelectrons. The NIST Database [7] gives the escape depth value about

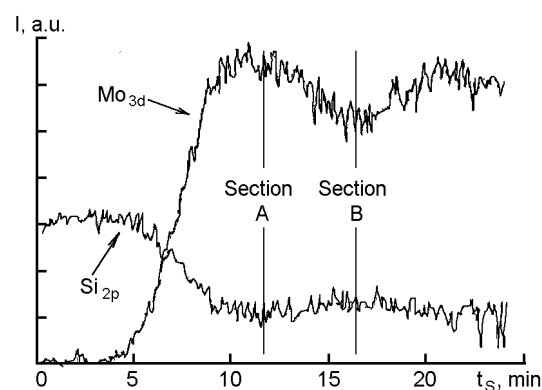


Fig. 2. XPS depth profile of as-deposited virgin Mo/Si multilayer.

Table 2. Layer thicknesses and densities in as-deposited Mo/Si multilayer obtained by TEM and LAXRD

	h , nm	ρ , g/cm^3
Si	6.19	2.3
Si-on-Mo	0.5	6.2
Mo	3.6	9.6
Mo-on-Si	0.95	6.2

3 nm for electron kinetic energy in the analyzed range. Fig. 3 displays the energy cross-section near $\text{Mo } 3d_{5/2}$ line corresponding to the points A (Fig. 3a) and B (Fig. 3b) of the depth profile. These characteristic points correspond to the middle of molybdenum and silicon layers. In our case, due to the large escape depth, in any point of the depth profile, we see the sum of the lines from pure element (Mo or Si) and the element in chemical compound (in mixed zones). Fig. 3 shows the curve fitting of Mo

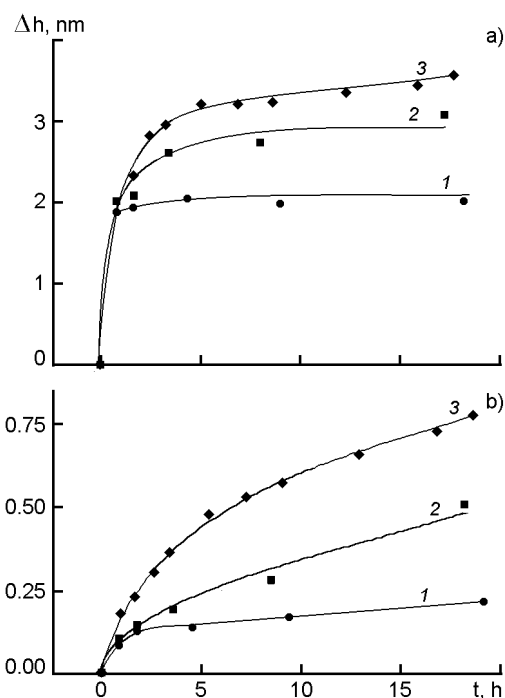


Fig. 3. Intensity of Mo $3d_{5/2}$ line (energy cross-section) after etching during 12 (a) and 17 min (b).

$3d_{5/2}$ peak for A and B points using Gauss-Laurence function. The peak consists of two components being peaks from molybdenum in the Si-on-Mo zone and pure Mo (point A). In the point B, this is the sum of the pure Mo peak and the peak in Mo-on-Si zone. In both cases, the binding energies of the components correspond to those of the references.

The shift of energy peak between points A and B is about 0.1 eV. This change of the total peak position is caused by change of intensity ratios of the components. The energy of the components is the same for point A and B. This means that chemical state of both mixed zones is identical and this is molybdenum silicide MoSi_2 . The diffusion mixing in Mo/Si multilayers becomes appreciable at annealing temperatures above 300°C . The thickness reduction of molybdenum and silicon layers and increasing thickness of the amorphous mixed zones is observed. It is well visible when comparing the TEM images in the initial condition (Fig. 1a) and after annealing (Figs. 1b and 1c). Diffusion of silicon atoms occurs through silicide layers (the mixed zones). Then, the chemical reaction of formation of MoSi_2 silicide [1] occurs at the mixed zone/molybdenum interface. This reaction proceeds with reduction of specific volume (volume of the generated silicide is less

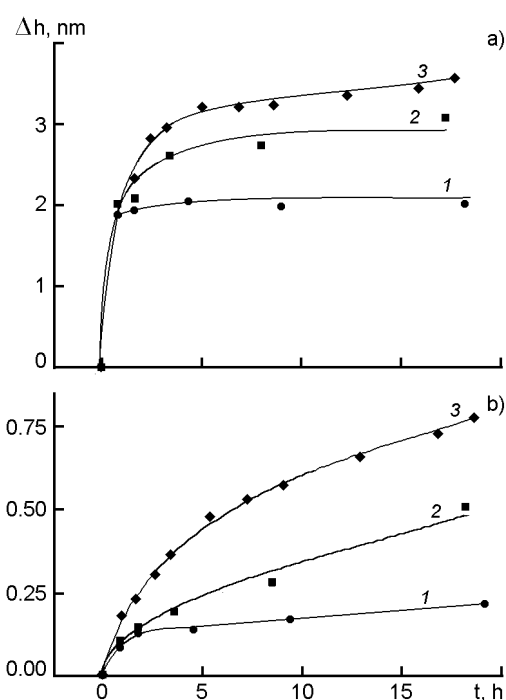


Fig. 4. Mixed zone thickness vs. annealing time for mixed zones: Si-on-Mo (a) and Mo-on-Si (b). Annealing temperature ($^\circ\text{C}$): 340 (1), 360 (2), 380 (3).

than total volume of molybdenum and silicon spent in the reaction). This results in reduction of the multilayer period.

A series of isothermal anneals has been performed at temperatures 340, 360, and 380°C . In Fig. 4, dependences of the mixed zone thickness vs. annealing duration are plotted. These dependences show some specific features. A considerable delay of Si-on-Mo mixed zone growth rate is observed after first several hours of annealing at all temperatures. It is possible to suppose that at reaching of some critical thickness, the growth of the Si-on-Mo zone practically stops, and this critical thickness increases as the annealing temperature rises. At the same time, the thickness of Mo-on-Si mixed zone continues to increase, and such sharp growth rate reduction is not observed at this interface. A specific feature of these dependences consists in that it is impossible to describe them using the classical expressions for diffusion, such as $h^2 \sim Dt$ (diffusion-controllable kinetics) or $h \sim kt$ (nucleation controlled by the chemical reaction rate) [8]. We did not manage to select any analytical expression which would describe well those dependences. This can be treated as a consequence of diffusion coefficient variations during annealing. As the diffu-

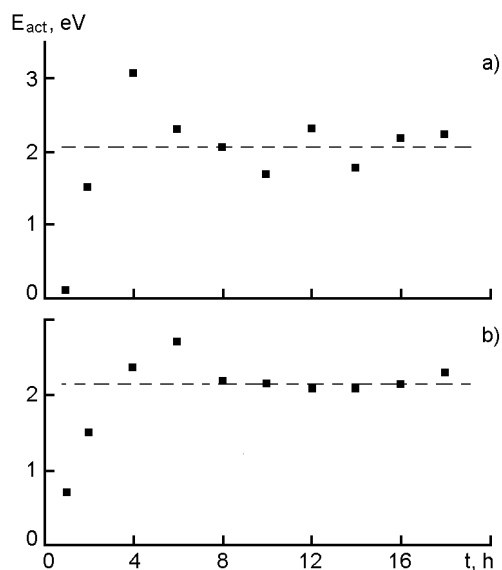


Fig. 5. Interdiffusion activation energy vs. annealing time for mixed zones Si-on-Mo (a) and Mo-on-Si (b).

sion coefficient depends on many parameters [8], any changes occurring in mixed zones at initial stages of annealing may result in a strong dependence of diffusion coefficient on the annealing time.

The value of activation energy could specify indirectly the one or another diffusion type. Unfortunately, as experimental dependences are not describable by the classical diffusion equation, we cannot determine the diffusion coefficient and construct the Arrhenius plot. However, assuming that D varies only slightly within each hour of annealing, it is possible to divide dependence into 1-hour sections and to approximate each one by a $h^2 \sim Dt$ dependence. Basing on these data, the Arrhenius plots for each mixed zone have been constructed, and dependences of activation energy on the annealing time for the Si-on-Mo and Mo-on-Si mixed zones have been obtained (Fig. 5). It is seen that the activation energy value for both zones varies considerably within first six hours of annealing. At initial stages, the activation energy values are 0.2 and 0.7 eV for the thin and thick mixed zones, respectively. Then the activation energy increases up to 2.1 eV, and do not change any more. The obtained diffusion activation energy value at late stages of annealing (2.1 eV) is close to the data from [3] (2.2–2.4 eV).

The observed dependence of activation energy can be due to a process which can be characterized as relaxation of an initial

state. The multilayer is formed by flow of high-energy particles in nonequilibrium conditions (deposition onto a cold substrate). So, formation a great number of nonequilibrium defects can be formed in layers, and especially at interfaces. At the initial annealing stages, when the mobility of interstitial atoms and vacancies increases, the ordering processes (recombination of vacancies and interstitials, etc.) occur. As a result, the concentration of vacancies decreases down to the equilibrium value. As diffusion in Mo/Si system occurs according to the vacancy mechanism, the ordering results in an increase of diffusion activation energy. It is of interest that the initial energy of activation for the thin mixed zone is essentially lower than for the thick one. This means that concentration of vacancies at the Si-on-Mo interface is essentially higher than at the Mo-on-Si one. This is obviously a consequence of different growth conditions at these interfaces. In case of amorphous silicon growth on polycrystalline molybdenum, much more defects (vacancies) are formed than when nanocrystalline molybdenum grows on amorphous silicon.

Thus, the chemical composition of amorphous mixed zones in Mo/Si multilayer coatings after deposition has been analyzed. It is shown that the mixed zones consist of $MoSi_2$ silicide. The of diffusion mixing in MoSi multilayer has been investigated. The distinction of mixed zones growth rate has been demonstrated. It can be explained by difference of Si-on-Mo and Mo-on-Si interface structure in as-deposited state. This difference appears as different activation energy of diffusion mixing for Mo-on-Si and Si-on-Mo interfaces.

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Особливості дифузійного перемішування у багат шарових покриттях Mo/Si

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За допомогою рентгенівської фотоелектронної спектроскопії, просвічувальної електронної мікроскопії та малокутової рентгенівської дифрактометрії досліджено дифузійне перемішування у багат шарових періодичних покриттях Mo/Si при виготовленні та нагріванні до 340–380°C. Показано, що у вихідному стані перемішані зони складаються з силіциду молібдену MoSi₂. Спостерігається відмінність у характері росту перемішаних зон у залежності від типу меж поділу (Si на Mo або Mo на Si). Встановлено, що енергія активації дифузії на початкових стадіях відпалу змінюється від 0.1 до 2.1 eV для межі першого типу та від 0.7 до 2.1 eV – для другого типу.