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# SILICIDE FORMATION IN A VACUUM-CONDENSED MOLYBDENUM—SILICON SYSTEM

N. S. Boltovets, V. A. Kravatskii, Yu. N. Makogon, S. I. Sidorenko, and N. N. Yaremenko

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The growing interest in the use of a high-melting metal (Mo, W. Nb) for the metallization of silicon is due to the creation of microelectronic devices, in which a layer of a high-melting metal that provides for the optimal transition characteristics and high adhesion to silicon can prevent the diffusion of silicon into the materials applied to the high-melting metal at high temperatures and current densities. On the other hand, the use of silicides of high-melting metals makes it possible to further reduce the dimensions of large integrated circuits and to shorten the delay times of signals [1].

These problems call for an investigation of the phase-formation processes in vacuum-condensed metal—silicon systems.

In the present work the influence of thermal treatment on the phase composition in the molybdenum—silicon system was investigated by an x-ray diffraction method (as in [2]).

Silicon with a (100) face parallel to the surface, a thickness equal to 350-370 μ, and a diameter equal to 60 mm served as the substrates. Their temperature was maintained equal to 520-570°K during the vacuum condensation.

The molybdenum was deposited in a dc triode system by the electron-beam, magnetron, and thermionic methods.

Two series of samples were prepared by the electron-beam method with a substrate temperature equal to 570°K. In the first series a layer of polycrystalline silicon with a thickness equal to 300 nm was deposited on preliminarily oxidized silicon single crystals, and then a layer of molybdenum with a thickness equal to 100 nm was condensed. In the second series molybdenum and silicon were deposited simultaneously at different rates from two sources in order to obtain a Mo:Si ratio equal to 1:2.

In both deposition variants the x-ray diffraction patterns obtained in Fe Kα radiation for the condensates in the original state showed only reflections from the single-crystal substrate and one diffuse halo at small angles of reflection (Figs. 1a and 2a). The complex type of variation of the electrical resistance with increasing temperature which is typical of amorphous materials [3] was discovered for the Mo films in the 293-820°K range. These data allow us to assume that the Mo films in the samples of the first series existed in the amorphous state.

Thermal treatment (annealing at 820°K for 2 h) of the samples of the first series does not cause changes in their phase composition (Fig. 1b), and the formation of $MoSI_2$ is detected after annealing at 920°K for 1 h (Fig. 1c).

In the samples of the second series the reaction resulting in the formation of $MoSI_2$ takes place after annealing at 820°K for 2 h (Fig. 2b), i.e., silicide formation occurs at lower temperatures than in the samples of the first series.

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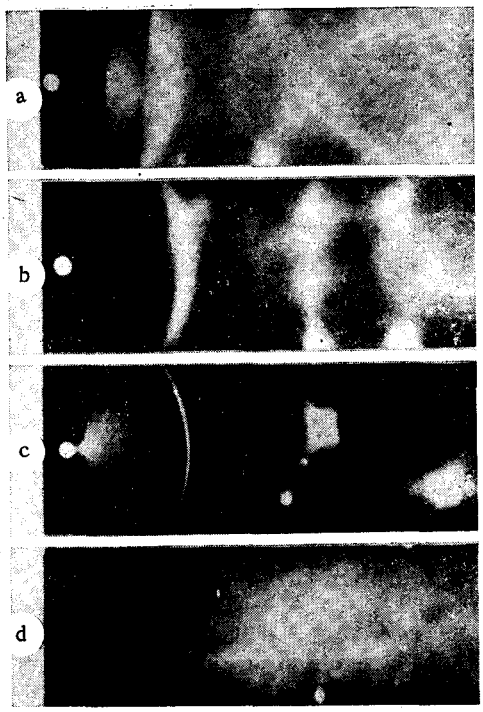


Fig. 1

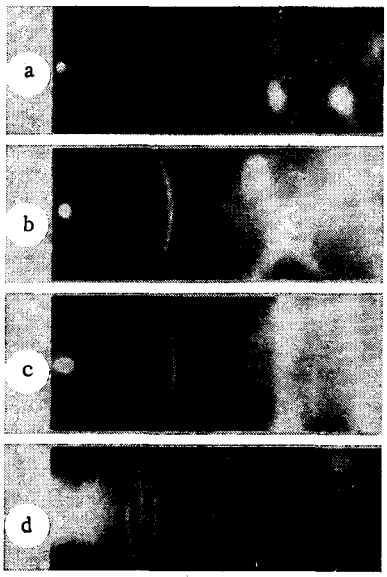


Fig. 2

Fig. 1. Debye powder patterns of Mo films with a thickness of 100 nm deposited by the electron-beam method on an oxidized layer of single-crystal silicon after sputtering (a) and annealing at 820°K for 2 h (b), at 920°K for 1 h (c), and at 1320°K for 15 min (d).

Fig. 2. Debye powder patterns of films with a thickness of 100 nm deposited on Si by the electron-beam method simultaneously from two sources (Mo and Si): a-d) see caption to Fig. 1.

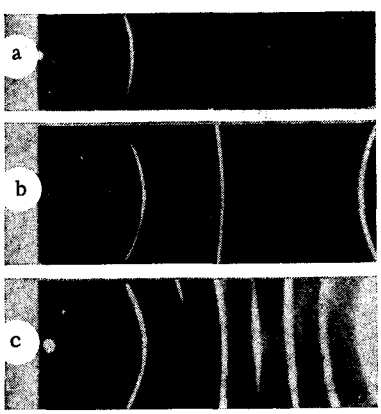


Fig. 3

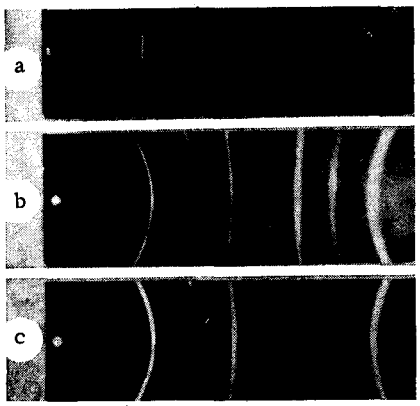


Fig. 4

Fig. 3. Debye powder patterns of Mo films with a thickness of 100 nm obtained by magnetron deposition on Si: a-c) see Fig. 1.

Fig. 4. Debye powder patterns of Mo films with a thickness of 100 nm obtained by deposition on Si in a triode system after sputtering (a) and annealing at 720°K for 2 h (b) and at 1320°K for 15 min (c).

At the same time, no x-ray diffraction reflections from a crystalline phase of Mo are detected after thermal treatment. Different grain diameters were observed in the samples from the two series after annealing at 1320°K for 15 min. As is seen from the x-ray diffraction patterns, in the samples from the first series the silicide $MoSi_2$ existed in the

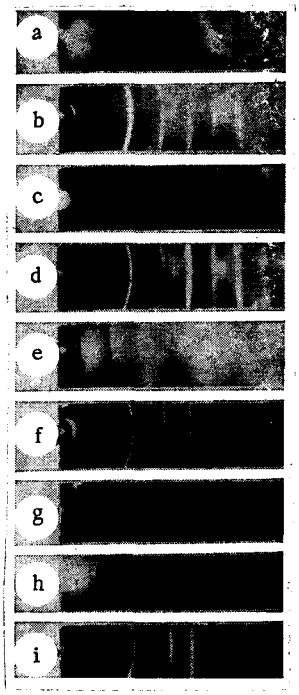


Fig. 5. Debye powder patterns of Mo films with a thickness of 100 nm sputtered by the thermoionic method with $V_b$ = 0 (a, e), 200 (b), 600 (c, g) and 900 V (d, h, i) before annealing (a-d) and after annealing at 820°K for 2 h (e-h) and at 1320°K for 15 min (i).

coarse-grain state, whereas in the case of the simultaneous deposition of Mo and Si, it existed in the fine-grain state (Figs. 1d and 2d).

Cracking of the coarse-grain samples was observed following the high-temperature annealing, apparently due to the large stresses appearing during silicide formation (compressive stresses in the $MoSi_2$ layer and tensile stresses in the substrate). In the case of the fine-grain state, the samples did not fracture.

In the third series of experiments a molybdenum layer with a thickness equal to 100 nm, which was deposited by magnetron deposition (sputtering in an argon medium, $T_{sub}$ = 520°K, p = 0.28 Pa) on single-crystal silicon, existed in a finely dispersed crystalline state. A bcc phase characteristic of solid molybdenum was observed by x-ray diffraction analysis. There was practically no texture in the films. Annealing at 820°K did not cause any changes in the phase composition.

The silicide-formation process in these samples took place during high-temperature heating at 1320°K: The x-ray diffraction pattern displayed reflections characteristic of $Mo_5Si_3$ and retained the intense maxima characteristic of Mo (Fig. 3c). The silicide formed existed in the finely dispersed state. Brief annealing at 1320°K (5 min) was insufficient for an Mo layer with a thickness of 100 nm to react completely with Si.

The x-ray diffraction investigations of Mo deposited on single-crystal silicon with a thickness of 370 μ ($T_{sub}$ = 523°K) in a triode system in an argon atmosphere (p = 0.2 Pa) (samples of the fourth series) revealed that the condensate is finely dispersed and has a bcc crystal lattice (Fig. 4). There was practically no texture. Heating of the samples to 720°K and holding for 2 h do not cause changes in the phase composition or the structure of the condensates (Fig. 4b). Changes are observed only after high-temperature annealing (15 min at 1320°K), at which the metal interacts with the silicon. However, the final product ($MoSi_2$) does not manage to form, and the intermediate silicide $Mo_5Si_3$ [4] in the finely dispersed state and a considerable quantity of unreacted molybdenum are detected on the x-ray diffraction patterns (Fig. 4c).

It seemed of interest to trace the changes in the phase composition in the Mo condensate—silicon system as the energy of the atoms of the material being deposited is varied. This could be accomplished in the case of the thermionic method of deposition, in which the layer being condensed is bombarded by the ions forming it during the condensation [5]. A layer of polycrystalline silicon with a thickness of 300 nm was deposited on preliminarily oxidized plates of single-crystal silicon (the thickness of the $SiO_2$ film was 0.5 μ) by the electron-beam method (the bias voltage on the substrate was $V_b$ = 0), and then a layer of Mo with a thickness of 100 nm was condensed by the thermionic method, $V_b$ being varied from 0 to 900 V.

It was established by x-ray diffraction investigations that the Mo condensates deposited at $V_b = 0$ exist in the amorphous state (Fig. 5a). The x-ray diffraction patterns of the samples obtained after deposition did not show the diffraction rings characteristic of the crystalline structure of molybdenum. Only reflections from single-crystal silicon were seen.

As the bias voltage on the substrate was increased from 200 to 900 V, the diffraction rings characteristic of the bcc crystal lattice of Mo appeared and became clearer (Figs. 5a-d). On the basis of the form of the Debye rings it may be concluded that the condensates exist in the finely dispersed state. There was practically no texture, and silicide phases were not detected in the samples of this series prior to annealing.

Additional annealing for 2 h at 820°K likewise does not result in the formation of silicide phases in amounts sufficient for them to be detected by x-ray diffraction analysis. Heating to 1320°K causes the appreciable occurrence of a reaction between molybdenum and silicon with the formation of $MoSi_2$. This is most clearly seen in the samples deposited with a large bias voltage (Fig. 5i). A considerable quantity of unreacted molybdenum is observed along with the finely dispersed silicide $MoSi_2$.

An fcc phase similar to that detected in [4, 6] in molybdenum condensates deposited by the electron-beam and thermionic methods was not observed in our investigations.

## CONCLUSIONS

Molybdenum films with a thickness of ~100 nm obtained after deposition on polycrystalline silicon by magnetron and thermionic methods, as well as after sputtering in a triode system have a polycrystalline structure with a face-centered crystal lattice, which is practically devoid of texture. The Mo condensates obtained after electron-beam deposition both in the case of deposition in a mixture with silicon and in the case of deposition on polycrystalline silicon were amorphous.

In the case of the deposition of condensates by the magnetron method or in a triode system (in both cases, the deposition of the high-melting metal took place in an argon atmosphere), the processes of silicide formation are slow in comparison to those in the samples obtained by sputtering in a vacuum either by the thermionic method or from two electron-beam evaporators.

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