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CVD CARBONYL THIN FILMS OF TUNGSTEN AND MOLYBDENUM AND THEIR SILICIDES - A GOOD ALTERNATIVE TO CVD FLUORIDE TUNGSTEN TECHNOLOGY

K.A. GESHEVA*, V. ABROSIMOVA** and G.D. BESHKOV***

*Central laboratory of Solar Energy and New Energy Sources, Bulgarian Academy of Sciences, 1784 Sofia, Bulgaria

**Institute of Physical Problems in Microelectronics Technologies, Academy of Sciences of USSR, 142432 Chernogolovska Moscow, USSR

***Institute of solid State Physics, Bulgarian Academy of Sciences, 1748 Sofia, Bulgaria

Abstract - By thermal decomposition of $W(CO)_6$ and $Mo(CO)_6$ at temperatures below 400°C and atmospheric pressure thin films on Si wafers were grown. This technology is shown to be an alternative to the fluoride one which uses WF_6 as a source material. Low resistivities together with a lack of erosion of Si substrate are possible. As-deposited films contain considerable amount of carbon and oxygen. By proper thermal annealing in H_2 atmosphere as well as by rapid thermal annealing in vacuum optimum conditions were found to obtain low resistive metal and metal silicides films. Auger electron spectroscopy and XRD-studies were used to show the connection between the chemical composition and structure of the two kinds of films on the one hand and their resistivities on the other.

1. - Introduction

The many advantages of CVD-tungsten films, most notably low resistivity, easy deposition, the ability to cover surfaces in a conformal way, high electromigration resistance, make them a key candidate as a material which is good for contacts, interconnections and multilevel metallization. Until now, so called fluoride CVD-tungsten technology has been used for deposition of W-thin films for microelectronics. Hydrogen reduction of WF_6 leads to deposition of films with thicknesses over a large range. Recent results however showed some limitations of this technology / 1 / . Because WF_6 reacts very strongly with silicon a considerable damage of the silicon wafer surface appears. An inter layer of silicides is usually necessary for deposition in order to compensate some of the negative sides of this technology. In spite of these disadvantages fluoride CVD-technology has been recently commercialized and it is considered that W-films application in VLSI devices is imminent.

We present in this paper a study of CVD-W and CVD-Mo films, the two based on another technological process; namely thermal decomposition of their corresponding carbonyls in an inert atmosphere. The absence of a corrosive gas in the processing gives the possibility of avoiding surface damage without using an intermediate silicide layer. From the literature this process is recommended as an alternative to the fluoride technology / 1 / .

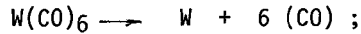
We have used in these experiments our experience of these materials with respect to solar energy applications / 2 - 4 / . We have studied so called black Mo and black W solar selective coatings which are actually composite structures - an oxide matrix with pure metal particles embedded in it. The basic difference between the black materials CVD process and the one studied in this paper is that now we do not intentionally involve an oxygen bleeding. We merely thermally decompose $W(CO)_6$ and $Mo(CO)_6$ in an Ar atmosphere.

2. - Deposition and measuring techniques.

All the samples under this study are deposited in horizontal CVD-reactor. The sublimator is immersed in a silicon oil bath, whose temperature is maintained with an accuracy of $\pm 1^\circ\text{C}$. The gas lines in the CVD system are PFA - Gatek type teflon tubes and fittings wrapped in heating tapes to keep the temperature of the vapour on the way to the reactor chamber equal or higher than the sublimator temperature. Silicon wafers with diameters of 50,8 mm and thickness of $(330 \pm 15) \mu\text{m}$ and $\rho = (42,5 \pm 62) \Omega \cdot \text{cm}$ were placed on a graphite susceptor and inductively heated by a high-frequency generator. Substrate temperature is measured by a Pt - Pt/Rh thermocouple, held in a channel in the susceptor. A thermoregulator, periodically switching off one of the three phases of the generator supply gives the possibility for the substrate temperature to be controlled with an accuracy of $\pm 10^\circ\text{C}$.

The source materials are of the type "for synthesis" purity (98 %). The gases used are Ar (99,95 %) and H_2 , used in the annealing process (99,99 %). All of them are additionally cleaned, using standard purifying and drying systems.

Thermal decomposition of $\text{W}(\text{CO})_6$ and $\text{Mo}(\text{CO})_6$ in an Ar atmosphere leads to a deposition of thin films on a heated substrate. The overall reactions can be written / 5 / :

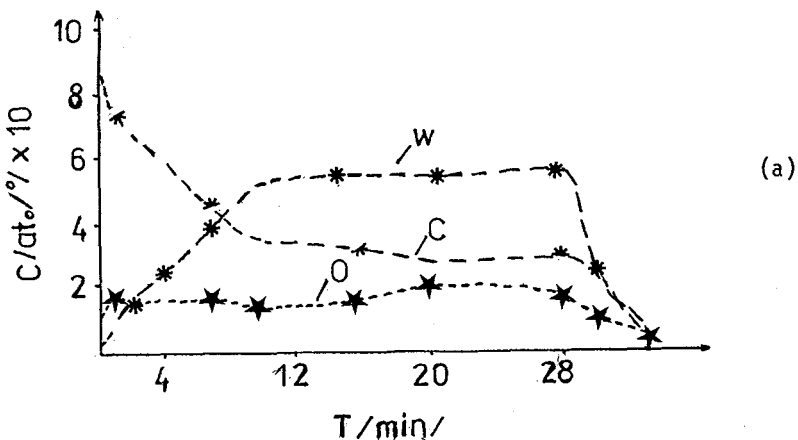


The deposition temperature for the two materials were in the range (300 - 400) $^\circ\text{C}$. The deposition rates were about 2 $\text{\AA}/\text{sec}$, the total gas flow - about 1500 cc/min.

The resistivity of the films was controlled by four-point probe techniques, using an automatic device FPP-100. Thickness of the films was measured by Talystep profilometer. Auger electron spectrometry and X-ray diffractometry were used for the composition and structure study.

3. - Results and discussions.

Decomposition of $\text{W}(\text{CO})_6$ and $\text{Mo}(\text{CO})_6$ below 400°C is incomplete and considerable amount of carbon and oxygen are usually found in the films besides the basic element W or Mo. If the process is carried out at a temperature above 400°C , powdery non-adherent films are deposited / 5 / . So, our samples were deposited below 400°C and carbides or oxycarbides rather than pure metal films were found to be deposited. As Auger analysis results show on Fig. 1 (a) and (b), about 30 % C and 20 % F are embedded in the film. For the Mo samples the oxygen content is higher than carbon content. It is seen, that films are homogeneous in composition through the film thickness, since atomic concentration versus sputtering time lines are almost flat through the depth of the films.



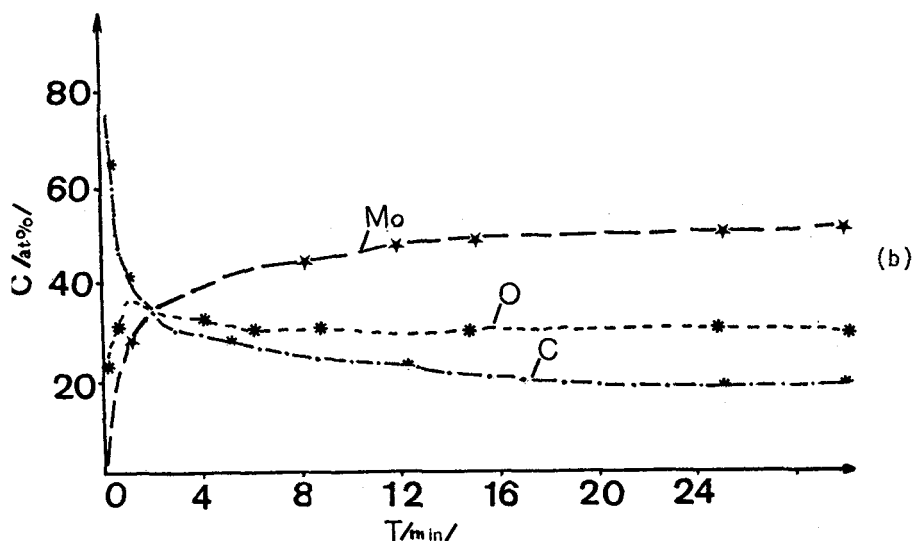
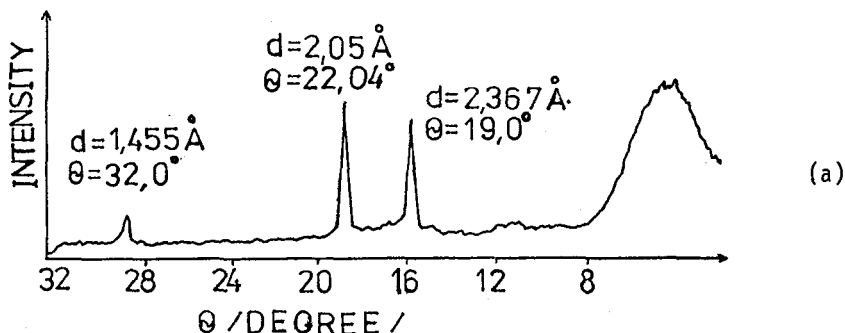


Fig. 1. Auger electron spectrometry analysis of as-deposited carbonyl CVD-W film (a) and CVD-Mo film (b), obtained by thermal decomposition of $W(CO)_6$ and $Mo(CO)_6$ at $340^\circ - 400^\circ C$.

Auger lines shapes and the known reactivity, especially for molybdenum with respect to oxygen and carbon, indicate that carbon and oxygen are probably bonded in the Mo lattice rather than being present in the film as molecular CO. In order to confirm this we studied the crystal phase structure of the films by X-ray diffractometry, using a copper tube and a proportional counter. Results for XRD spectra are presented on Fig. 2. - for as-deposited W (a) and Mo (b) films.

The observed maxima in (a) correspond to a crystalline phase with d-spacing of: 2,37; 2,05; 1,46 which are lines of modified $W_2(CO)$ phase, for which the theoretical data are respectively 2,44; 2,12; 1,49. In the case of as-deposited Mo film we see a weak diffraction pattern of probably a crystal phase of MoC with distorted d-spacing of 2,34; 2,25; 2,10, compared to the theoretical data: 2,44; 2,29; 2,12. Further we obtained different sets of samples from W and Mo with different thicknesses in order to study the influence of the post deposition annealing on the electrical resistance of the films. The measured sheet resistance of as-deposited W and Mo films for different thicknesses is of the order of 25 to 250 Ω/\square . In order to decrease the resistance of these films we performed a post deposition annealing, using our CVD



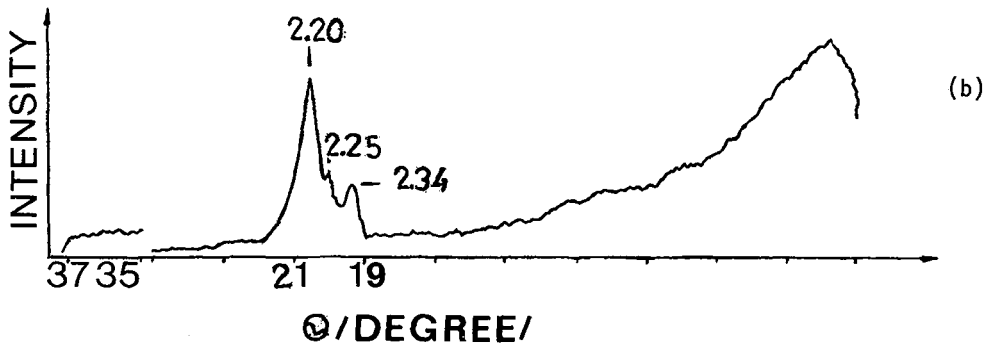


Fig. 2. XRD - analysis of as-deposited carbonyl CVD-W (a) and CVD-Mo (b). Cu K radiation.

system reactor and the same way of heating, merely increasing the generator power and reaction temperature close to 800°C. In fact we did a solid phase reduction of as-deposited films in H₂ atmosphere. An optimized duration of 10 min and the total flow-rate of 880 cc/min argon and hydrogen were established. Together with the compositional and structural studies we measured the sheet resistance as well as the resistivity of the films in order to find the influence of the annealing process. The results are shown in Table 1 for two kinds of material (w and Mo) and for different thicknesses of the films.

TABLE 1. Electrical sheet resistance and resistivity of as-deposited and annealed carbonyl CVD-W and CVD-Mo thin films.

TUNGSTEN FILMS											
d	Annealed in H ₂					Rapid thermal annealed films					
	R _S	ρ	R _S	ρ	R _S	800°C	1200°C	1300°C	ρ	R _S	ρ
μ	Ω/□	Ω.cm	Ω/□	Ω.cm	Ω/□	Ω.cm	Ω/□	Ω.cm	Ω/□	Ω.cm	Ω.cm
0,6	14,7	8,8x10 ⁻⁴	0,559	0,34x10 ⁻⁴	-	-	-	-	-	-	-
0,3	17,3	5,2x10 ⁻⁴	0,575	0,17x10 ⁻⁴	-	-	-	-	-	-	-
0,21	22,8	4,8x10 ⁻⁴	-	-	12,15	2,55x10 ⁻⁴	1,08	0,173x10 ⁻⁴	-	-	-
0,16	26	4,3x10 ⁻⁴	-	-	14	2,3x10 ⁻⁴	1,015	0,163x10 ⁻⁴	-	-	-
0,12	134	16,1x10 ⁻⁴	3,23	0,39x10 ⁻⁴	-	-	-	-	-	-	-
MOLYBDENUM FILMS											
0,3	16,2	4,86x10 ⁻⁴	0,530	0,159x10 ⁻⁴	-	-	-	-	-	-	-
0,19	23,5	4,5x10 ⁻⁴	-	-	18,5	3,52x10 ⁻⁴	-	-	0,407	0,077x10 ⁻⁴	-
0,13	27,5	3,58x10 ⁻⁴	-	-	22	0,726x10 ⁻⁴	-	-	6,35	0,84x10 ⁻⁴	-
0,12	32,26	3,87x10 ⁻⁴	15,7	1,87x10 ⁻⁴	-	-	-	-	2,2	0,26x10 ⁻⁴	-

At present, the conclusions which we make on the basis of the table data are as follows:

The two kinds of as-deposited films have resistivities of the order of several hundred microohms per cm. After annealing in H₂ atmosphere, the resistivity falls markedly and in some cases to less than 20 μΩ.cm; the lowest for W was 17 μΩ.cm and for Mo - about 16 μΩ.cm. Going to a higher annealing temperature in vacuum we succeeded in decreasing the resistivity of Mo films to the value of 7,7 μΩ.cm, compared with the bulk value for Mo of ρ = 5,77 μΩ.cm. We should note that films annealed at 1300°C in vacuum look perfect, compared to ones, heated in H₂. The high sheet resistance and the corresponding resistivity for as-deposited films can be considered

as a function of two factors: impurities in the grain boundaries and the grain size / 6,7 /. Our as-deposited films are small grained, polycrystalline, with grain size about 500 Å. During the annealing, dependent on O and C contents, sometimes grains can grow considerably. The influence of the impurities in carbonyl films on structure and electrical properties has been studied in detail / 8 /. Auger analysis of the annealed films were performed and the results are shown on Fig. 3. - (a) for tungsten films and (b) for molybdenum ones. Even though most of the carbon and oxygen leaves the film, from Fig. 3. it is seen that films still contain carbon and oxygen. This is important since a practical process must tolerate some impurities in a strongly reactive material, such as W and Mo. It is encouraging that the low resistivity of CVD-W and CVD-Mo films is not affected by excessive purity. Although not measured, chemical composition of such films may still contain some impurities, since a fully annealed Mo film contains 3 % O and 1 % C, besides 96 % Mo / 8 /. We see that in annealed films a considerable amount of Si has appeared, obviously coming from the Si substrate, during the high temperature annealing. On Fig. 4 (a) and (b)

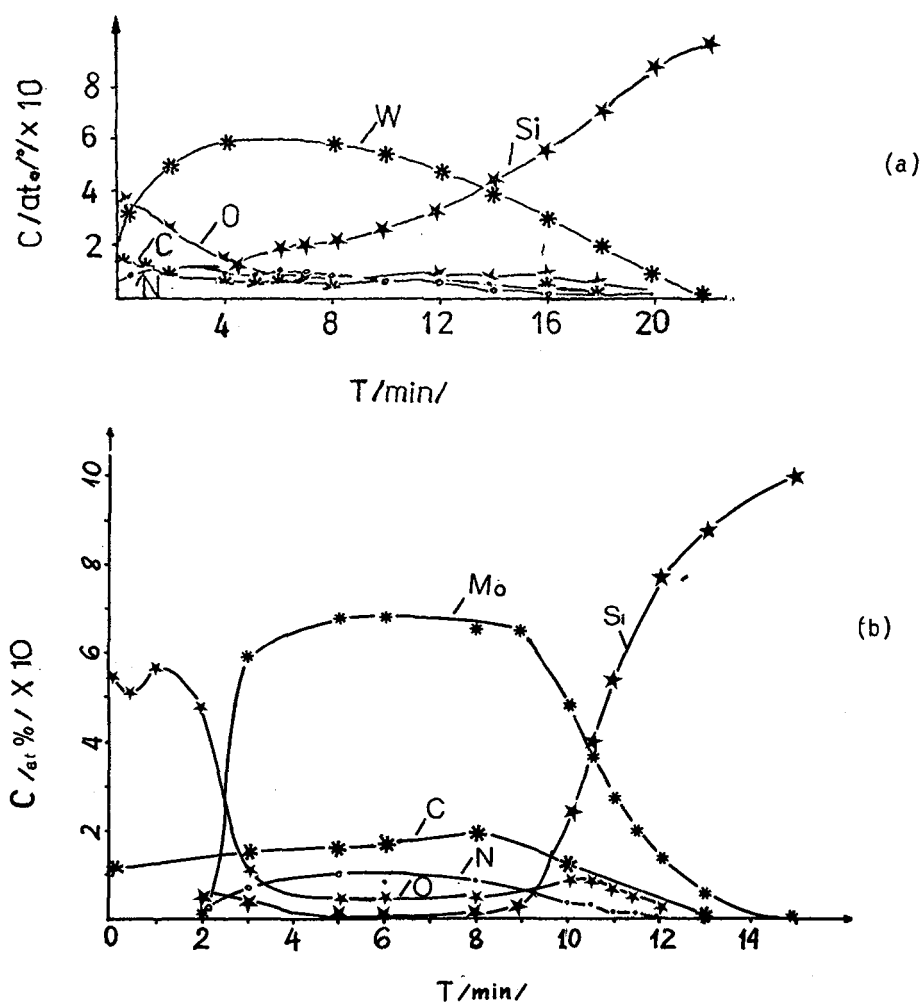


Fig. 3. Auger electron spectrometry analysis of annealed at 780°C carbonyl CVD-W film (a) and carbonyl CVD-Mo film (b) in H₂ atmosphere.

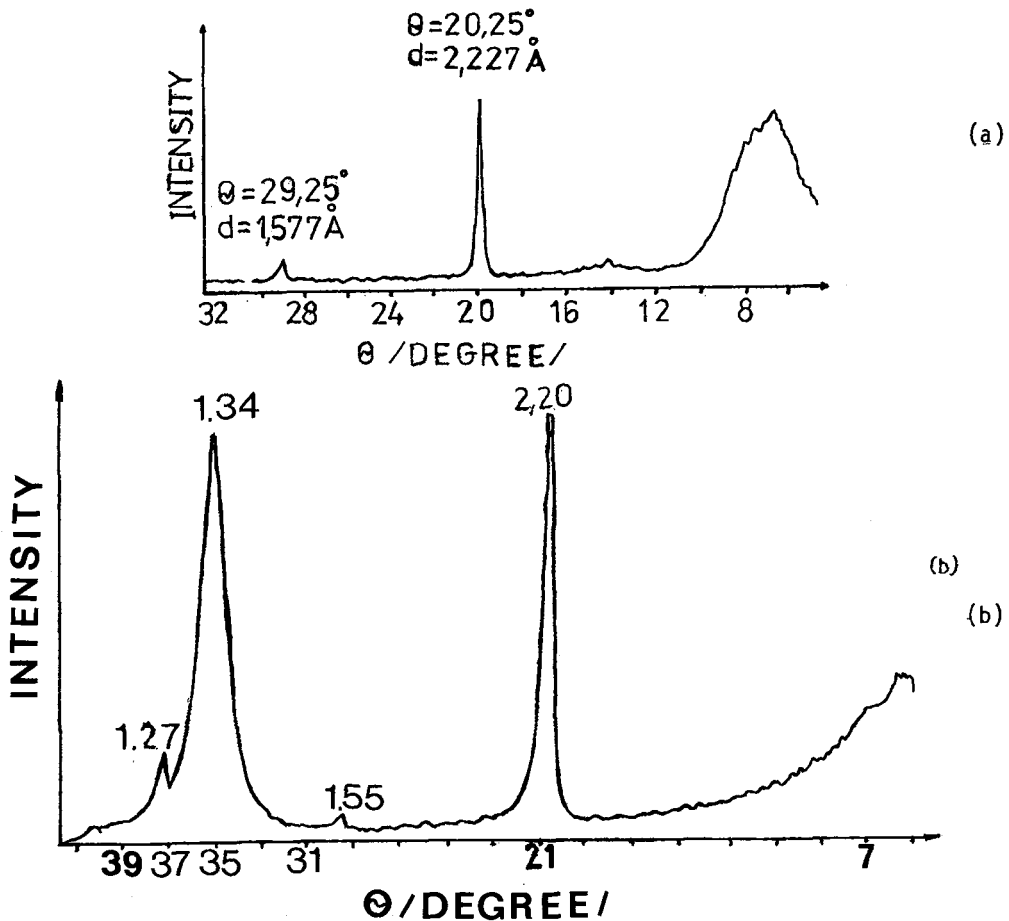


Fig. 4. XRD - analysis of annealed carbonyl CVD-W (a) and CVD-Mo (b) films at temperature of 780°C for 10 min.

we have shown the results from XRD analysis of annealed films and we see that although a great amount of Si is found in the W film, no peaks in the XRD spectrum other than of pure metallic W are found. At the same time in the case of Mo we see besides some of the pure Mo lines (2,23; 1,57; 1,29) an other strong peak (1,34) of Mo_3Si (2,19; 2,00; 1,36). Probably Mo is easier to alloy with Si than W. We tried to study higher temperature annealing for our films and to find the temperature at which W silicides would appear. Very recent XRD - study of W films, annealed at 1200°C in vacuum for 30 sec showed that at this temperature alloying of W and Si is possible. This will be a subject for future detail study.

We have also studied by replica electron microscopy techniques the Si surface, on which carbonyl W film has been deposited and further chemically etched. As the study showed besides some non-etched points, probably of the W film, no other defects could be noticed - Fig. 5.

5. - Conclusions

By thermal decomposition of $\text{W}(\text{CO})_6$ and $\text{Mo}(\text{CO})_6$ and by further optimum annealing, it is possible to obtain low-resistive materials. One important advantage of the carbonyl

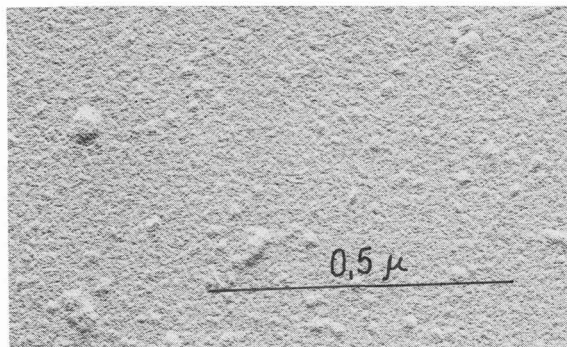


Fig. 5. EM replica of Si surface, on which W film has been deposited and further etched. \times Magnification 100 000 X.

CVD-process is the lack of attack on the Si surface. The fact, that silicides are formed at annealing temperature may be useful in decreasing the contact resistance of the metal films to p^+ and n^+ of Si. In addition an annealing temperature of less than 800°C is compatible with microelectronics technology.

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