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RAPID THERMAL ANNEALING OF CVD-MOLYBDENUM THIN FILMS

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Abstract. Molybdenum thin films deposited in silicon by thermal decomposition of $Mo(Co)_6$ at atmospheric pressure have additionally undergone a rapid thermal annealing (RTA) in argon atmosphere. Their surface resistance and specific resistivity have been studied in dependence of the annealing temperature.

Резюме. Тонкие слои из молибдена, полученые методом термического осаждения из газовой фазы $Mo(Co)_6$ после получения были подвергнуты быстрому термическому отжигу в аргоновой атмосфере и было исследовано его влияние на поверхностное и удельное сопротивление образцов.

1. Introduction

Intensive studies of VIb group transition metals as prospective materials for metalization in microelectronics technology have been done in the last 15 years. Tungsten thin film technology based on hydrogen reduction of WF_6 have been largely investigated with respect to its advantages, most notably selectivity of deposition, conformal coverage, low resistivity and high electromigration resistance, as it is reported by Green [1]. A part of the results show some of the limitations of CVD-fluoride technology. Because, WF_6 as a source material, reacts very aggressively with Si, the growth of CVD-W films can be accomplished by excessive erosion of Si, encrichment and "worm-hole" formation. Often this deterioration can be avoided by interlayers such as silicides what makes the technology more expensive and not flexible.

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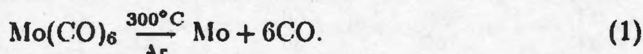
In some of our previous studies, Gesheva et al. [2] reported for W films, deposited by pyrolytical decomposition of $W(CO)_6$ and further annealed in hydrogen atmosphere. Studying the Si surface, the authors found no deteriorations.

In the present study we used $Mo(Co)_6$ as a source material. The basic reaction, which take place, is as follows:



$$Mo(CO)_6 \xrightarrow[Ar]{300^\circ C} Mo + 6CO. \quad (1)$$

The process of pyrolytical decomposition of $Mo(CO)_6$ in presence of oxygen has been intensively studied with respect to their application as solar selective surfaces. Chain et al. [3,4] have used in their study stainless steel substrates and further their films have been partially annealed in H_2 atmosphere in order to obtain composite structure, namely oxide matrix in which pure metal particles are embedded. Going to fully annealing Garver [5] obtains highly reflective Mo films with low resistivities. The previous experience we applied to obtain Mo films on Si substrates and to study their properties with respect to application in microelectronics metalization.

2. Experimental

Resistivity study was carried out using a four-point probe technics — Model FPP-100. Auger analyses were performed by Auger electron spectrometry system in the Institute of Microelectronics, Sofia, X-ray diffraction analyses were made in Chernogolovka.

The RTA was performed in the Institute of Technological Problems in Chernogolovka, Moscow area, using halogen lamps, which heat the samples for 60 s in Ar flow atmosphere.

3. Results and Discussion

A set of samples with thickness (d) in the range 0.02 – 0.15 μm was used. X-ray diffraction patterns for all of them show that they are with amorphous structure before the RTA treatment. Auger analyses show that besides Mo, films contain a great amount of oxygen and carbon. Carbon may originate from CO groups, although CO bond at the temperature of deposition (300–400°C) seems unlikely to be broken. Another source of carbon may be the CVD system which includes a vacuum pump, seal connections and so on.

Table 1. Sheet resistance R_s and resistivity ρ of as-deposited CVD-carbonyl Mo films

No of sample	Thickness d, μm	Surface resistance R_s, $\Omega/\square$	Resistivity ρ, $\mu\Omega$.m
11	0.055	119.8	6.59
4	0.02	19.27	2.89
7–1	0.02	143.4	2.87
7–2	0.02	196.0	3.92
7–3	0.02	160.4	3.2
7–4	0.02	164.3	3.29

Table 2. Surface resistance R_s and resistivity ρ of CVD-carbonyl Mo films after Rapid Thermal Annealing

No of sample	Temperature T, °C	Duration t, s	Atmosphere	Surface resistivity R_s, Ω/□	Resistivity ρ, μΩ.m
11	600	60	Ar	70.38	3.87
11	700	60	Ar	35.18	1.93
11	800	60	Ar	23.44	1.29
4	600	60	Ar	17.14	2.571
4	700	60	Ar	14.48	2.172
4	800	60	Ar	9.204	1.381
4	900	60	Ar	1.402	0.21
4	1000	60	Ar	0.784	0.117
7–1	600	60	Ar	138.6	2.77
7–1	650	60	Ar	137.6	2.75
7–1	700	60	Ar	130.2	2.6
7–1	750	60	Ar	56.24	1.12
7–1	800	60	Ar	39.4	0.788
7–2	700	60	Ar	163.2	3.26
7–3	750	60	Ar	82.86	1.66
7–4	800	60	Ar	37.04	0.74

Results for sheet resistance are resistivity of Mo films before and after RTA treatment are presented in Table 1 and Table 2. As it can be seen from the tables films as thin as 200 Åhave enough high density to expose sheet resistance in the range of about 3 up to 6.6 $\mu\Omega m$. These values drop down considerably when RTA

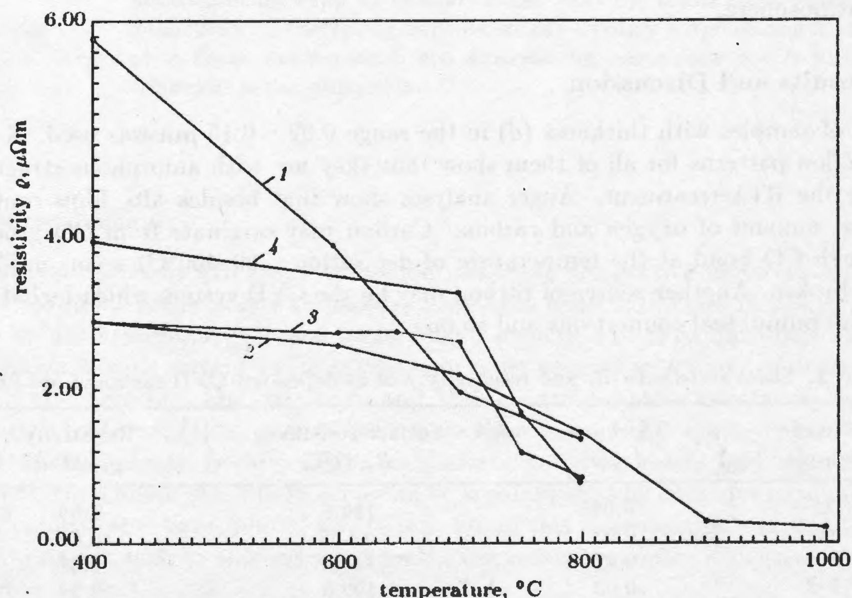


Fig. 1. Resistivity versus RTA-temperature for Mo thin films with different thicknesses: *1* — $d = 0.055$ μm; *2* — $d = 0.15$ μm; *3* and *4* — $d = 0.02$ μm

is applied. Results are obvious, looking at Fig. 1, where temperature dependence of resistivity ρ is presented. As it can be seen, for films showing comparatively higher resistivity when as-deposited, temperature of 600°C leads to a great decreasing, while for as-deposited films with lower resistivity the latest change very slightly after RTA for temperatures up to 650°C. Temperatures higher than this one influence strongly the resistivity of the films. Temperatures over 800°C further decrease resistivity, but they cannot fit to the microelectronics technology. The lowest resistivity obtained is 0.117 $\mu\Omega$.m, when bulk Mo has resistivity of 0.056 $\mu\Omega$.m.

Auger results for chemical composition distribution through the thickness of the films show that low resistivities are not tied to an excessive purity. Even after annealing films still contain some quantities of C. Because of the existence of C, acting as an inhibitor for the grain growth during the thermal annealing, after the treatment films are still with small grain structure. This effect we have observed even in the case when performing annealing for longer periods (about 10 min at $\sim$ 700°C [2]. We also would like to note that no aging effects in the films are observed, measuring R_s long after RTA treatment.

4. Conclusion

The obtained results show that by pyrolytical decomposition of $Mo(CO)_6$ at atmospheric pressure and argon atmosphere, followed by further annealing by RTA, it is possible to deposit very low resistive material for metalization. At the same time, films are with good uniformity, they adhere well to Si substrates and have high density in order to possess low resistivities at small thicknesses.

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