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INTERMIXING IN IMMISCIBLE MOLYBDENUM/COPPER MULTILAYERED METALLIZATION UNDER EXCIMER LASER IRRADIATION

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Copper metallization of semiconductor devices requires reliable diffusion barriers against interaction of Cu with Si substrate. Molybdenum is assumed to be the possible solution because Mo/Cu is an immiscible metallurgical system. In this paper the intermixing between Mo and Cu under XeCl excimer laser irradiation was studied. The samples were prepared by magnetron sputtering in the form of Mo/Cu multilayers. The thickness of Mo barriers was 20 nm, the total thickness of Cu in $Si/SiO_2/Mo/(Cu/Mo)\times n$ (n=1, 2, 5 and 10) samples was 1 μm. The samples were irradiated at the fluences of F=0.5, 0.8, 1 and 1.4 Jcm^{-2} in vacuum and in nitrogen at the pressure of $1.1x10^5$ Pa with N=100, 1000 and 10 000 laser pulses. Analyses were performed using Rutherford backscattering spectrometry, X-ray diffraction (XRD) and resistometry. The time dependence and the depth profile of the temperature in the samples under irradiation was numerically calculated. From the results it follows that even after irradiation by the laser fluence high enough to melt copper, only Mo and Cu XRD peaks were observed. In this way the immiscibility in the Mo/Cu system seems to be verified for the non-equilibrium laser processing. The intermixing between the Mo barriers and the Cu layers as well as the SiO_2 underlayer was decreased by the presence of reactive gases, namely oxygen incorporated into molybdenum. The irradiation of the Mo/Cu structure in nitrogen was thermally more effective than in vacuum due to the different coupling of the laser beam with the structure originating from the surface reactions and/or modifications.

1. Introduction

Copper is studied extensively as a potential substitute for aluminum in the metallization of semiconductor devices. Its resistivity is lower in comparison with the Al-alloy

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values and it has higher electromigration reliability [1]. However, copper brings about some problems not met with aluminum, like corrosion, oxidation, diffusion, reaction with silicon, and poor adhesion to SiO_2 [1-4]. These metallurgical problems impose the need of reliable diffusion barriers. The barriers for the Cu based metallization were summarized by Wang et al. [5]. The most reliable one is $Ta_{36}Si_{14}N_{50}$. Molybdenum with low bulk resistivity of 5.3 $\mu\Omega$cm has been studied seldom up to now. It was shown that magnetron sputtered Mo is an effective barrier in the Mo/Cu multilayers up to the 600 °C/1h annealing in vacuum [6] and in the Si/Mo/Cu structures up to the 500 °C/1h annealing in hydrogen [7].

Mo/Cu as well as Ta/Cu or W/Cu are immiscible, non- continuous systems composed from metals with different crystalline structures (e.g. bcc/fcc for Mo/Cu). They are more stable and much less mutually soluble than miscible, structurally coherent combinations, like Ni/Cu [8]. From the phase diagram measurements it follows that the solubility of Mo in Cu is vanishingly small at 900 °C and the solubility of Cu in Mo is 1.5 wt% at 950 °C. These systems are immiscible both in the solid and liquid states [9].

In the Cu metallization technology XeCl excimer laser recrystallization was successfully applied to increase the grain size in the Cu film up to a few μm [10,11] or to fill the contacts and interconnect trenches [12]. In both cases pulsed laser melting and resolidification process typical for nanosecond XeCl laser regime was employed. Under such conditions the advantage of the immiscible Cu/barrier combination is obvious. Moreover, the interfaces in immiscible layered structures are sharp [13].

With respect to the discussed potential advantages, Mo/Cu metallization with Mo barrier was chosen for the XeCl laser irradiation study in this work. The experimental structures were prepared as the Mo/Cu multilayers (Mo/Cu/Mo/Cu .../Mo) which allow for redundancy against electromigration damage [14]. Nevertheless, in this paper only laser annealing results are reported. Another advantage of multilayered structures is the possibility to correlate effectively the interdiffusion with the resistance increase under annealing.

2. Experimental details

The samples under study were magnetron sputtered onto thermally oxidized Si(100) wafers with the SiO_2 thickness of 0.5 μm. For sputtering the Ar gas of 4N5 purity was used. The samples were perpared in the two different regimes but at the same deposition rates. The first set of the samples (A) was deposited in higher starting vacuum $\leq 2\times10^{-5}$ Pa and at lower working gas pressure of $(3\text{-}5)\times10^{-1}$ Pa. For the second set (B) the starting vacuum and working gas pressure were 4×10^{-5} Pa and $(4\text{-}7)\times10^{-1}$ Pa, respectively, i.e. more residual reactive gases were present in the sputtering chamber. The differences between the A and B runs in the composition of the Mo barriers having lower or higher content of oxygen and nitrogen, respectively, were expected.

The Mo barriers 20 nm thick were deposited as bottom- and upper- layers of 1 μm thick Cu layer at first and then in the following depositions copper was divided by additional Mo barriers of the same thickness into 2, 5, and 10 sublayers 0.5 μm, 0.2 μm and 0.1 μm thick, respectively, to increase the number of the Mo/Cu interfaces. Thus,

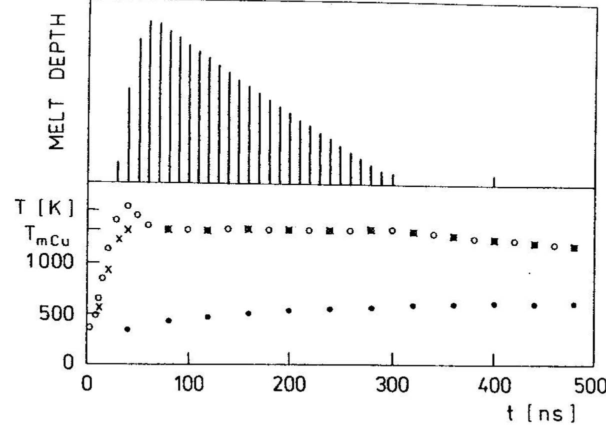

Fig. 1. Results of the calculation of the depth of melting (a) and temperature time and depth profiles (b) of the 1Cu sample irradiated by one XeCl laser pulse with the fluence 1.4 Jcm^{-2} and duration of 30 ns. z is the depth in the sample, T_{mCu} is the melting point of copper (1356 K).

four types of the samples were prepared. They will be denoted as 1Cu, 2Cu, 5Cu, and 10Cu according to the number of the Cu layers. Additionally, single Mo and Cu layers with various thicknesses were prepared to provide the resistance reference values for the resistometry measurements.

The samples were processed by an XeCl laser (Lambda Phys. LPX 315 i) in the vacuum of 5×10^{-3} Pa or in IC grade purity nitrogen at overpressure of 1.1×10^{5} Pa at the fluences of F=0.5, 0.8, 1 and 1.4 Jcm^{-2}. N=100, 1000 and 10 000 laser pulses were directed to the same irradiation site. The pulse duration was 30 ns, the repetition rate was 50 Hz.

Samples were analyzed using Rutherford backscattering spectrometry (RBS) with 2 MeV He^+ ions and X-ray diffraction (XRD) using CuK_α radiation. The concentration profiles of the elements in the samples were obtained by the simulation of RBS spectra [15]. For the resistometry measurements at room temperature the four point probe was used.

3. Calculation of temperature evolution

The time dependence and the depth profile of the temperature in our samples were calculated using the well known procedures [16]. Some results are summarized in Tab. 1 and for the sample 1Cu and F=1.4 Jcm^{-2} they are illustrated in Fig. 1. The temperatures were calculated in the depths corresponding to the middle of both Mo barriers and in the Si substrate 10 nm below the interface with SiO_2. From Fig. 1 it follows that Cu melts only at the fluence $\geq$1.4 Jcm^{-2} and Mo remains solid (even for F=1.9 Jcm^{-2}). The depth of melting does not depend significantly on the number of Mo

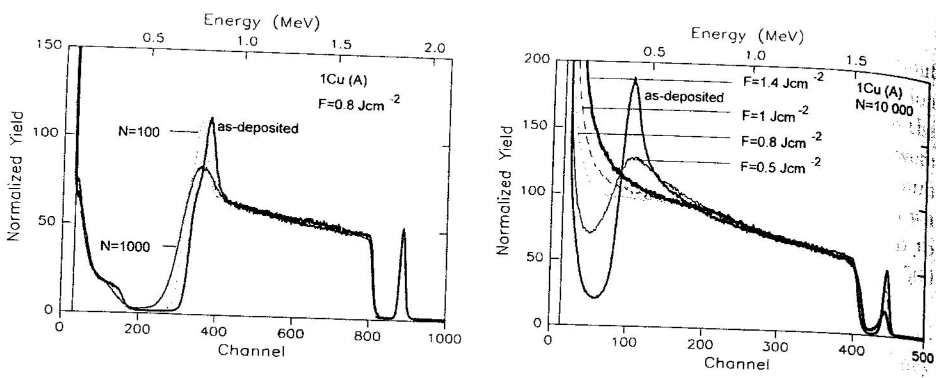

Fig. 2. RBS spectra of the 1Cu (A) sample: (a) as-deposited and irradiated in vacuum at $F=0.8$ Jcm^{-2} and with N=100 and 1000 pulses; (b) as-deposited and irradiated in N_2 ambient at F=0.5, 0.8, 1 and 1.4 Jcm^{-2} and with N=10 000 pulses .

barriers. Therefore, we expect that in 1Cu sample the Cu layer is melted incompletely, in 2Cu sample the first upper Cu layer is melted, in 5Cu sample three upper layers of Cu and in 10Cu sample seven upper layers of Cu are melted. Assuming that the heat from the irradiated samples is conducted away into the substrate [10], an effective grain growth in the Cu layers via melting and solidification processes is expected in the samples 2Cu, 5Cu. 10Cu, because here the recrystallization could start at the interfaces providing the heterogeneous nucleation site. These results are valid for the first laser pulse. The subsequent pulses find the surface in a modified state, with increasing roughness, i.e. decreasing reflectivity. Therefore, the subsequent pulses could have more influence than the first one and the melting may be deeper.

At the repetition rate of 50 Hz and at the cooling rate obtained from the calculations the irradiation of our samples could be considered as a sequence of thermally independent pulses. However, this is true if the modification of the samples during irradiation is not considered. The results of our calculation are in agreement with the paper [12] where the fluence for melting of 1 μm thick Cu film by XeCl laser is between 0.8 and 1.6 Jcm^{-2}.

4. Results and discussion

A different behaviour of the upper and bottom Mo barrier was found in the 1Cu (A) sample from the A series. The reaction of the bottom Mo with the underlying SiO_2 as well as with the Cu overlayer is documented in Fig. 2. A broadening of the Mo/SiO_2 interface appeared at $F=0.8$ Jcm^{-2} and N=1000 pulses for the vacuum irradiated samples (Fig. 2a). Obviously, the temperature of the sample increased with increasing number of pulses. A similar behaviour was observed for the N_2 irradiated sample. With increasing fluence the reaction is completed as can be deduced from the smearing out of the RBS spectra for $F\geq0.8$ Jcm^{-2} (Fig. 2b).

The reaction of the refractory metal films with SiO_2 during the high temperature heat treatment was studied thoroughly (e.g. [17]). Due to the presence of metallic

Table 1. Results of temperature evolution calculations for 1Cu and 2Cu samples. F-fluence of laser pulse, T_{max} - max. temperature in a given depth z in the sample, Δz_{max} - max. depth of melting of Cu (Δz_1 - for 1Cu, $\Delta z_{1,2}$, for 2Cu with two Cu layers numerated downwards), Δt_m- duration of melting of Cu.

Sample	F [J cm^{-2}]	T_{max} [K] for following values of z [nm]				Δz_{mmax} [nm]		Δt_m [ns]
1Cu		z=10	z=1030	z=1550		Δz_1		
	1	1320	1260	> 480		0		0
	1.4	1570	1385	> 600		780		285
	1.9	1970	1670	> 730		1000		650
2Cu		z=10	z=530	z=1050	z=1570	Δz_1	Δz_2	
	1	1310	1260	1240	> 500	0	0	0
	1.4	1570	1410	1405	> 620	500	260	280
	1.9	1980	1700	1660	> 690	500	500	> 480

Table 2. Heats of formation of molybdenum silicides and oxides [20]

Silicide	Heat of formation [kJ/g. atom]	Oxide	Heat of formation [kJ/g. atom]
$MoSi_3$	- 33.5	MoO_2	-543
Mo_5Si_3	- 58.5	MoO_3	-752
$MoSi_2$	-117		

atoms the Si-O bonds are broken and new metal-O and metal-Si bonds are formed. The thickness of the SiO_2 layer decreases as the reaction proceeds. Generally, it is assumed that temperatures of $\geq$800 °C are necessary to start the reaction. (However, for the Ti/SiO_2 couple the reaction at the temperatures of $\geq$400 °C was observed [18]). According to our experimental data on the Cu/Mo multilayers annealed in vacuum the reaction at the Mo/SiO_2 interface appeared at the annealing of $\geq$700 °C/1 h [19]. The temperatures near the Mo/SiO_2 interface in our laser irradiated samples are $\geq$1260 K for the fluences of $\geq$1 Jcm^{-2} (Tab. 1). Therefore, an interaction at the Mo/SiO_2 interface resulting in the formation of molybdenum silicides and molybdenum oxides can be expected. Some compositions and corresponding heats of formation of silicides and oxides which can be formed at the Mo/SiO_2 interface are given in Tab. 2 [20]. The formation of the $MoSi_2$ silicide and the MoO_3 oxide is the most probable. The XRD patterns do not reveal the presence of a crystalline Mo silicide or Mo oxide in our samples (Fig. 3). We assume that amorphous mixtures of Mo-Si and Mo-O were formed at the interface. This is not surprising at the cooling rates $\geq10^8$ K/min (favourable for the amorphous phase formation) obtained at the excimer laser irradiation.

The upper Mo barrier in the samples of the A series is more stable that the bottom one (Fig. 2). Here, the reactions of Mo with Cu underlayer and with the ambient gases are to be considered. Some intermixing between the upper Mo and Cu layer

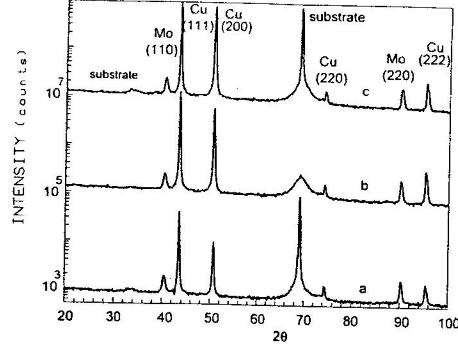

Fig. 3. XRD pattern of the 1Cu (A) sample: (a) as-deposited, (b) irradiated at F=1.4 Jcm^{-2} and with N=10 000 pulses in vacuum, (c) irradiated at F=1.4 Jcm^{-2} and with N=10 000 pulses in N_2 ambient.

Table 3. Sheet resistance [Ω] of sample 5Cu (B) after various irradiations by XeCl laser beam in vacuum and nitrogen. (F - fluence)

F	Irradiation ambient					
	Vacuum Number of pulses			Nitrogen Number of pulses		
[J cm^{-2}]	10^2	10^3	10^4	10^2	10^3	10^4
0.8	0.024	0.027	0.027	0.024	0.025	0.027
1.0	0.025	0.026	0.028	0.026	0.027	0.029
1.4	0.025	0.025	0.024	0.025	0.026	0.026

appeared for both vacuum and N_2 (Fig. 2b) irradiations at N=10 000 pulses for all fluences. For the stability of the Mo barrier the content of oxygen and nitrogen may be decisive (c.f. [21]). The gases could build into the samples during deposition, room temperature storage and laser irradiation. In Figs. 4 and 5 the concentration profiles of O, Mo and Cu obtained from RBS spectra for the samples irradiated in vacuum and nitrogen ambient are shown. The content and distribution of oxygen does not change significantly due to various irradiations. (Some redistribution of oxygen in the sample is observed in Fig. 5.) Hence, the main source of oxygen seems to be the deposition process and contamination during a few-week storage at the atmospheric pressure before laser irradiations. It is interesting that the concentration profiles of Cu and Mo are significantly broader for the irradiations in N_2 (Fig. 5). This effect will be discussed later.

As follows from the XRD measurements, e.g. Fig. 3, only the Mo and Cu peaks are found in the irradiated samples. This is in agreement with the immiscibility of Cu and Mo. We assume that the intermixing at the Mo/Cu interface is due to the grain boundary diffusion, considering also the mixing between Mo and liquid-Cu in some

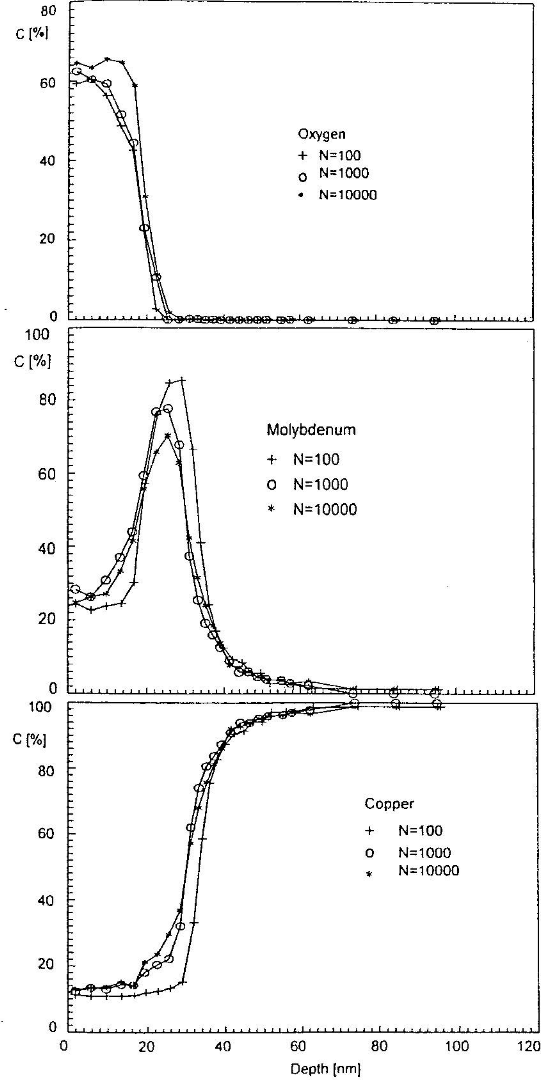

Fig. 4. Concentration profiles of oxygen, molybdenum and copper of 1Cu (A) sample irradiated at F= 1.4 Jcm^{-2} and with various numbers of pulses in vacuum.

cases. From our calculations in Chap. 3 it can be concluded that the time, during which the temperature of the sample is high enough for diffusion, is ≈10 ms at N=10 000 pulses. Supposing the typical value of the grain boundary diffusion coefficient of 10^{-10} cm^2s^{-1}, the diffusion length $l = 2\sqrt{Dt} \cong 10$ nm is obtained. It is comparable with the Mo barrier thickness. Hence, the diffusion based intermixing at the Mo/Cu interface seems to be reasonable.

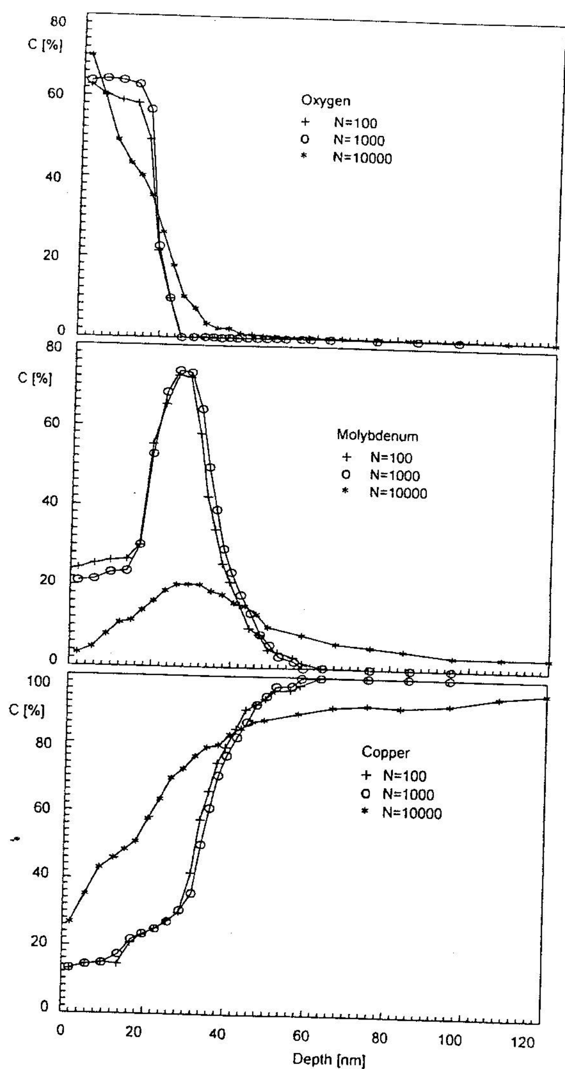

Fig. 5. Concentration profiles of oxygen, molybdenum and copper of 1Cu (A) sample irradiated at F= 1.4 Jcm^{-2} and with various numbers of pulses in N_2 ambient.

From Fig. 6 a slight loss of the surface barrier in the N_2 irradiated sample in comparison with the vacuum irradiation is evident. At F≥1 Jcm^{-2} sometimes the yellow colour of the underlying copper was seen in the optical microscope or even by the naked eye. Some volatile Mo-N or Mo-O compound (compounds) may cause this effect. It should be mentioned that in our previous paper [19] Mo_2N and MoN were identified after the nitrogen furnace annealing of the Mo/Cu samples. The loss of the upper Mo and the disclosure of the Cu layer with lower reflectivity (R_{Cu} = 30%, R_{Mo} = 45% at

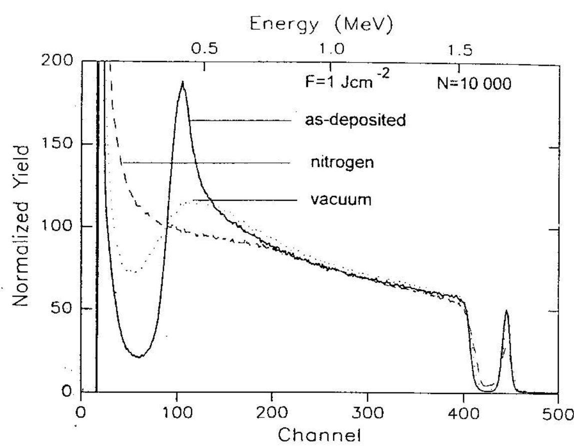

Fig. 6. RBS spectra of the 1Cu (A) sample: as deposited, irradiated at F=0.8 Jcm^{-2} and with N=10 000 pulses in vacuum and in N_2 ambient.

the wavelength 308 nm of the XeCl laser) may explain also the broadening of the Mo and Cu concentration profiles observed for the nitrogen annealing (Fig. 5). However, a more effective coupling of the laser beam with the sample may be also due to the roughening of the surface.

In the samples of the B series again some intermixing at the upper Mo/Cu interface was observed both at the vacuum as well as at N_2 annealings (Fig. 7a). However, it was less distinct than for the samples of the A series (Fig. 7b). Here, also the intermixing at the inner interfaces and at the Mo/SiO_2 interface is suppressed. We assume that due to the incorporation of more reactive gases (O_2, N_2) into the samples of the B series during deposition the integrity of the Mo barrier and the layered structure is conserved. This was observed even for F=1.4 Jcm^{-2}, where three upper Cu layers are melted. There are no significant differences between the Mo RBS peaks for the layers coming into contact with liquid Cu and solid Cu, respectively. This is of some importance for recrystallization of Cu via pulsed excimer laser melting and solidification. The RBS spectra of our sample are shifted in the manner that corresponds to the hypothetical expansion or shrinkage (densification) of the layered structure under irradiation (Fig. 7). These processes can be explained by the different temperature evolution of internal stresses for different irradiation conditions.

The XRD spectra of the samples from the B series (Fig. 8) are similar to those of 1Cu (A) (Fig. 3). Again only the Mo and Cu peaks were found. In this way the immiscibility in Mo/Cu system is verified. For the as-deposited sample a texture of both Mo and Cu layers can be detected. A tendency for the texture of the Cu increases with decreasing of Cu layer thickness. After the laser irradiation the textures are lost for both Mo and Cu layers.

Some typical results of the resistance measurements for the sample 5Cu (B) corresponding to Fig. 7 are shown in Tab. 3. In the as-deposited state the sheet resistance

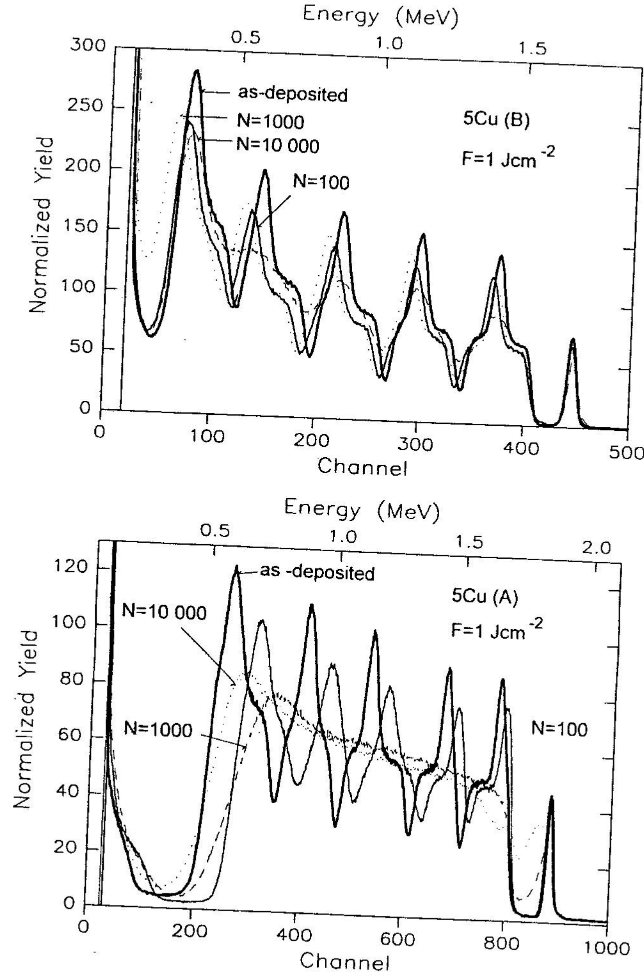

Fig. 7. RBS spectra of: (a) 5Cu (B) sample in as-deposited state and after irradiation in N_2 at F=1 Jcm^{-2} and with N=100, 1000 and 10 000 pulses; (b) 5Cu (A) sample in the as-deposited state and after irradiation in N_2 at F=1 Jcm^{-2} and with N=100, 1000 and 10 000 pulses.

of this sample is 0.023 Ω. The resistances of the single Mo layer 20 nm thick and Cu layer 200 nm thick are 9.55 Ω and 0.0975 Ω, respectively. The resistance of the sample 5Cu (B), calculated as parallel combination of the single layer resistances, is 0.0192 Ω. The measured value is higher because the interface scattering is not considered. After the laser irradiations the samples showed only small and non-systematic change of resistance. Obviously, various effects like outgasing, intermixing at the interfaces, material loss and recrystallization of Cu at the highest fluence may be responsible for

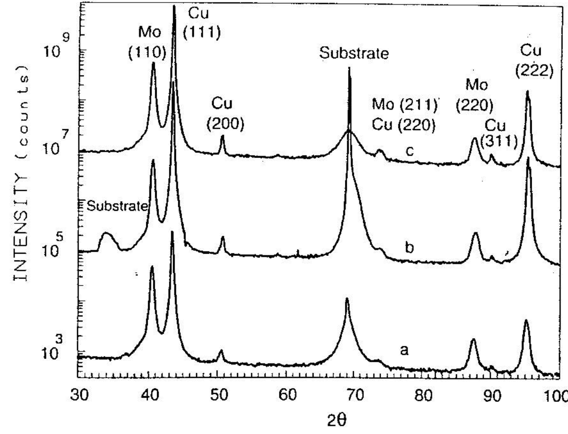

Fig. 8. XRD pattern of the 10Cu (B) sample: (a) as-deposited, (b) irradiated at F=1.4 Jcm^{-2} and with N=10 000 pulses in vacuum, c) irradiated at F=1.4 Jcm^{-2} and with N=10 000 pulses in N_2 ambient.

the resistance fluctuations.

5. Conclusions

From the calculations of the temperature time and depth profiles in our Mo/Cu multilayered metallization structures it follows that the Cu layer (layers) melts at the laser fluence of F=1.4 Jcm^{-2}. Under these conditions only the Mo and Cu peaks were found by XRD. Thus, the metallurgical immiscibility of the Mo-Cu pair seems to be verified even for the highly non-equilibrium laser melting and solidification processes. The intermixing at the Mo/Cu interfaces is explained by the grain boundary diffusion.

The reactions between the bottom Mo barrier and the underlying SiO_2 layer as well as intermixing of upper and internal Mo barriers with Cu layers were effectively decreased by the presence of reactive gases, mostly oxygen, incorporated into molybdenum during the deposition and/or storage at the atmospheric pressure. In this way the favourable effect of stuffing the metallic barriers by reactive gases was verified.

Some losses of the upper Mo barrier and the disclosure of the Cu underlayer at the irradiation in nitrogen is attributed to the formation of the volatile Mo compounds. Here, the laser annealing could be thermally more effective because of better coupling of the XeCl beam with Cu than with Mo.

Molybdenum with a reasonable content of reactive gases (mostly oxygen) seems to be an effective barrier for the Mo/Cu metallization submitted to the laser recrystallization of copper via the liquid state.

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