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Ellipsometric study of ion implanted copper surface and its room temperature oxidation

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The room temperature oxidation of ion-implanted copper surface has been studied ex situ and in situ using ellipsometry. The ellipsometric parameters Ψ and Δ were measured at light incidence angle 75° for different wavelength values in the range of 280 to 760 nm using averaging both over two azimuthal zones and single one. The oxide layer was removed from the copper surface during the aluminum ion implantation an then the growth of the newly formed oxide film on the ion implanted surface was studied by ellipsometry. Basing on the spectroellipsometric data, the oxide film thickness has been calculated for two types of copper oxides.

Проведены эллипсометрические исследования окисления при комнатной температуре ионно-имплантированных поверхностей меди. Эллипсометрические параметры Ψ и Δ измерены при угле падения света 75° для различных величин длины волны света в области 280–760 нм с усреднением как по двум, так и по одной азимутальным зонам. Оксидная пленка с поверхности меди удалялась в процессе ее имплантации ионами алюминия, а затем рост вновь формируемой пленки оксида меди на имплантированной поверхности исследован эллипсометрическим методом. Проведены на основе спектроэллипсометрических данных расчеты толщин пленок для двух типов оксидов меди.

Due to its unique physical properties, copper in modern technology is used in a wide set of the devices starting from electric contacts in microelectronic apparatus (Cu thin films) to bulk mirrors for powerful laser system for plasma diagnostics [1, 2]. The conductive copper layer used in the elements of microelectronics is characterized by thickness of the order of 1 μm. That is why the problem of the layer protection against corrosion is still actual. The implantation of aluminum and nitrogen ions has been proposed to that aim. This work is aimed at solution of a problem connected with corrosion resistance enhancement of the copper films by ion bombardment without deterioration of electrical and optical characteristics thereof.

Copper was evaporated onto a 7.6 cm diameter single crystalline silicon wafer coated with approximately 100 nm thick thermally grown silicon dioxide film. The copper layer thickness was approximately 400 nm. The pressure during evaporation was $7\cdot10^{-4}$ Pa. The sample was cut into several pieces to perform ion implantation by Al ions (dose: $1.4\cdot10^{17}$ ion/cm^2, $U = 140$ kV), N^{2+} ions (dose: $1\cdot10^{14}$ ion/cm^2, $U = 240$ kV) and N_2^+ molecular ions (dose: $5\cdot10^{15}$ ion/cm^2 and $1\cdot10^{16}$ ion/cm^2, $U = 100$ kV). The implantation was performed using the Heavy Ion Cascade ion implanter at the KFKI Campus

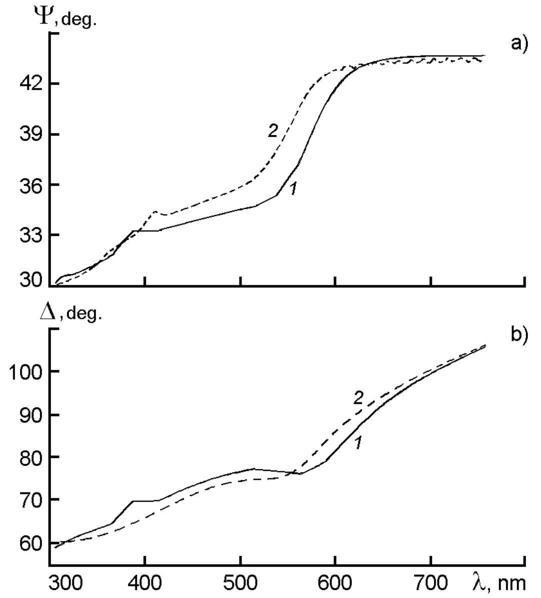

Fig. 1. Generated and experimental spectra of ellipsometric parameters of copper surface immediately after ion implantation (model with Cu_2O layer): *1*— Model Fit, *2* — Exp E 75.1°.

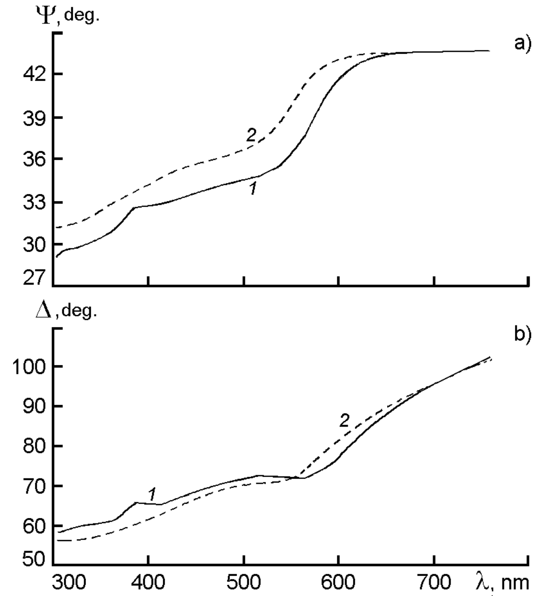

Fig. 2. Generated and experimental spectra of ellipsometric parameters of the same implanted copper surface after 11 days later (model with Cu_2O layer):*1*— Model Fit, *2* — Exp E 75.1°.

in Budapest. The surface properties of copper film were studied using spectral and angular ellipsometry, atomic force microscopy (AFM), and Fourier transform infrared (FTIR) reflectometry.

The copper surfaces were studied by means of variable incidence angle spectroscopic ellipsometry (VASE, J.A.Woollam, USA), within the probing photon energy range $h\nu$ from 1 to 4.70 eV in rotating analyzer mode. The ellipsometer was operated in autoretarder mode as described in [3] for the case of Fe corrosion studies. The data were acquired and evaluated by WVASE® software. The main feature of the ellipsometric technique is the measurement of the change in the polarization state of light reflected from the sample. This is expressed by angle Δ, phase shift between orthogonal components of the electromagnetic wave reflected from the sample, and Ψ, azimuth of the restored linear polarization, $\rho = \tan\Psi\exp(i\Delta)$. Here, ρ is the ratio of the complex reflection coefficients for light polarized in parallel $p(r_p)$ and perpendicular $s(r_s)$ directions to the plane of incidence, $\rho = r_p/r_s$. Details of this technique have been described elsewhere [4]. The determination error of the ellipsometric parameters in our experiments was within the range ±0.25 to ±0.15° for Δ and ±0.13 to ±0.07° for Ψ at 90 % confidence limit.

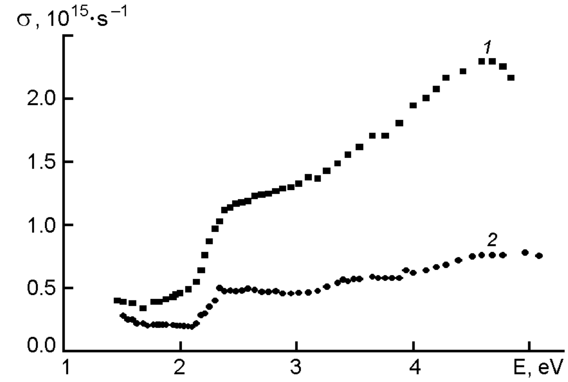

Fig. 3. Optical conductivity spectra for as deposited Cu film (*1*) and after stay in air atmosphere (*2*).

On the other hand, Δ and Ψ were obtained within incidence angle of laser beam from 50 to 85° using single wavelength (632.8 nm) multiple incidence angle ellipsometry.

The calculated Δ(φ) and Ψ(φ) curves for non-implanted sample were obtained using three different optical models. In the first model, the number of free parameters during fitting procedure was only one, the Cu_2O film thickness. In the second model, a physical mixture of copper and voids was supposed to be the film material. The number of free parameters was two, the film thickness and the percentage of void volume

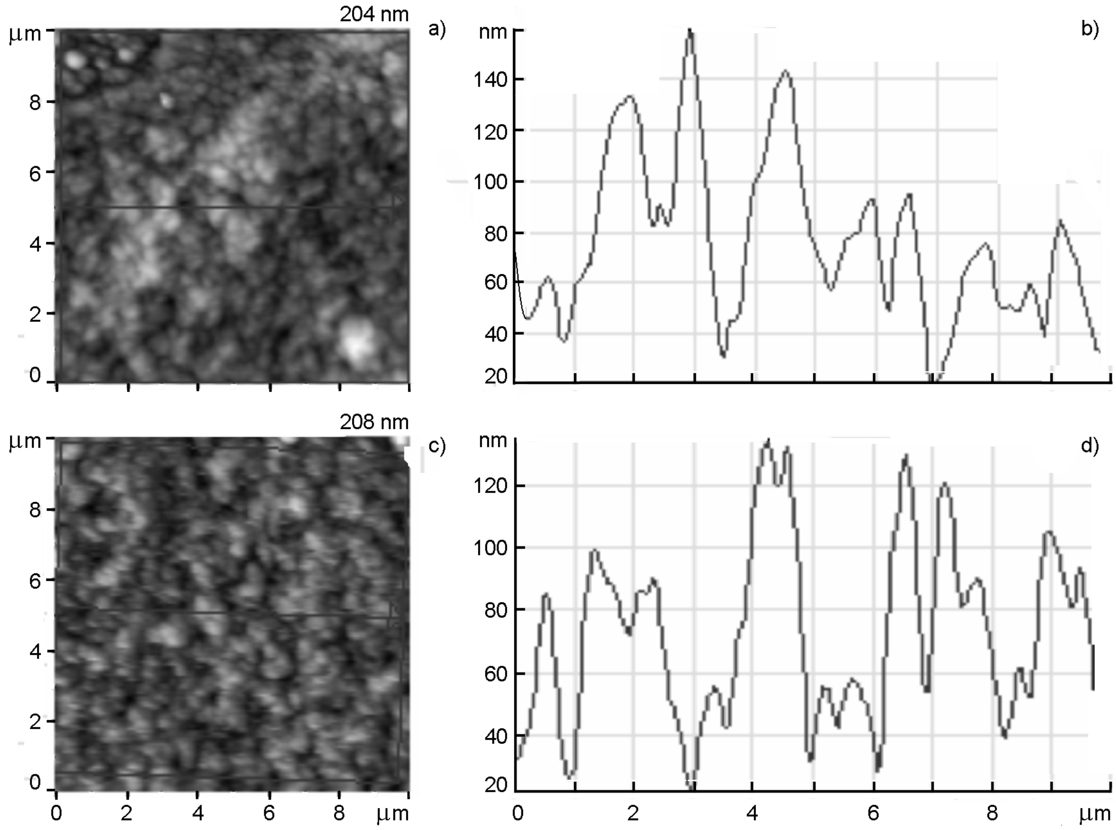

Fig. 4. The atomic force microscopy data (a, c) and the averaged profile (b, d) on the probed surface for Cu films before the ion irradiation (a and b respectively) and after the irradiation by N^{2+} ions (c, d).

therein. The Bruggeman effective medium approximation was applied to calculate the effective dielectric function of the film. The third model was based on the assumption that the film on the surface consists of Cu_2O and Cu. The number of free parameters was two, the film thickness and the percentage of Cu in the Cu_2O material. The film thickness was obtained to be 4.4 nm and the film composition, 91 % Cu_2O and 9 % Cu. For this optical model, the measured and the calculated $\Delta(\varphi)$ and $\Psi(\varphi)$ curves show an excellent agreement.

From spectro-ellipsometric measurements of Δ and Ψ performed on the non-implanted sample, the thickness values of CuO and Cu_2O oxide layers were evaluated as 5.7 nm and 4.0 nm, respectively.

After finishing the aluminum ion implantation, the native oxide layer formed before on the copper surface was sputtered of. This was found from evaluation of spectra $\Delta(\lambda)$ and $\Psi(\lambda)$ measured on ion-implanted Cu sample immediately after the sample removal from the implantation chamber. Evaluations evidenced a rather low thickness values of CuO and Cu_2O oxide layers (0.08 and 0.04 nm, respectively (Fig. 1)). This means that the very high dose ion implantation removed the native oxide layer film from the surface of Cu film.

11 days later, spectro-ellipsometric measurements performed on the same implanted sample have shown that the thickness of CuO and Cu_2O oxide layers amounted 2.2 nm and 1.5 nm, respectively (Fig. 2). These values provide a thickness estimation of the native oxide layer formed during 11 days. Thus, owing to Al ion implantation, the native oxide layer on copper surface is smaller than that on non-implanted sample.

Optical conductivity spectra for as-deposited Cu film and after its storage in air are shown in Fig. 3 (E is the photon energy). It is seen that optical conductivity of Cu sample stored in air decreases within the ultraviolet region at least 2 times in comparison to those for as-deposited Cu film due to formation of thin oxide layer on the surface.

It has been shown by calculations that the penetration depth for N^{2+} ions of the above-specified energies is 440 nm, it corre-

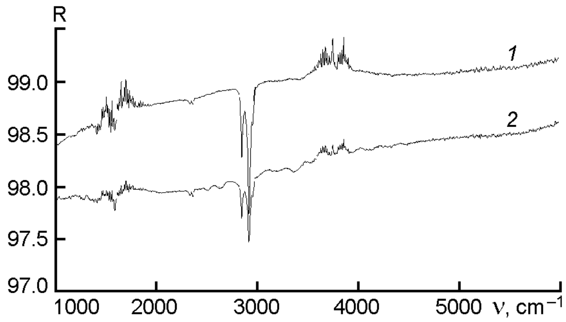

Fig. 5. Spectra of the reflection in IR region for unirradiated (curve *1*) and irradiated (curve *2*) areas of the Cu film surface.

sponds to the copper/SiO_2 interface. Using the AFM technique, it was determined that the films are rough. The roughness parameters are the same for irradiated and unirradiated Cu films (Fig. 4). This evidences the optimal choice of the N^{2+} ion energy to provide the high adhesion level of such films on the Si substrates without significant modification of their surface. However, it was determined that the Cu films are not continuous as it was obtained using optical microscopy technique, because the absorption bands at of 2844 and 2926 cm^{-1} are observed by means of the IR reflection technique. These bands correspond to IR absorption by the SiO_2 substrate (Fig. 5).

Thus, when modeling the subsurface region of ion implanted copper, two layers, such as a native copper oxide and 250 μm thickness ion implanted layer, must be taken into consideration. Due to ion implantation, the native oxide layer on copper surface is smaller than one on non-implanted sample.

References

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Еліпсометричні дослідження іонно-імплантованої поверхні міді та її окиснення при кімнатній температурі

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Проведено еліпсометричні дослідження окиснення при кімнатній температурі іонно-імплантованих поверхонь міді. Еліпсометричні параметри Ψ і Δ виміряно при куті падіння світла 75° для різних величин довжини хвилі світла в області 280–760 нм з усередненням як за двома, так і за однією азимутальними зонами. Оксидна плівка з поверхні міді розпилювалась у процесі її імплантації іонами алюмінію, і наступний ріст нової плівки оксиду міді на імплантованій поверхні досліджено еліпсометричним методом. На основі спектроеліпсометричних даних розраховано товщину плівок для двох типів оксидів міді.