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Ion implantation induced by Cu ablation at high laser fluence

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Abstract

High energy laser plasma-produced Cu ions have been implanted in silicon substrates placed at different distances and angles with respect to the normal to the surface of the ablated target. The implanted samples have been produced using the iodine high power Prague Asterix Laser System (PALS) using 438 nm wavelength irradiating in vacuum a Cu target. The high laser pulse energy (up to 230 J) and the short pulse duration (400 ps) produced a non-equilibrium plasma expanding mainly along the normal to the Cu target surface. Time-of-flight (TOF) technique was employed, through an electrostatic ion energy analyzer (IEA) placed along the target normal, in order to measure the ion energy, the ion charge state, the energy distribution and the charge state distribution. Ions had a Boltzmann energy distributions with an energy increasing with the charge state. At a laser fluence of the order of 6×10^6 J/cm^2, the maximum ion energy was about 600 keV and the maximum charge state was about 27+.

In order to investigate the implantation processes, Cu depth profiles have been performed with Rutherford backscattering spectrometry (RBS) of 1.5 MeV helium ions, Auger electron spectroscopy (AES) with 3 keV electron beam and 1 keV Ar sputtering ions in combination with scanning electron microscopy (SEM). Surface analysis results indicate that Cu ions are implanted within the first surface layers and that the ion penetration ranges are in agreement with the ion energy measured with IEA analysis.

Keywords: Laser ablation; Plasma laser; Ion implantation; RBS analysis; AES analysis

1. Introduction

Intense laser pulses irradiating solid targets generate hot plasmas with high temperature and high density. Plasma expands in vacuum at supersonic velocity along the normal to the target surface accelerating electrons, ions and neutrals. At a laser power density of the order of 10^{15} W/cm^2 the plasma temperature reaches values higher than 10 keV and the plasma density is of the order of 10^{19} cm^{-3}, as obtained by interferometric investigations recently reported in literature [1–3]. Plasma contains ions at high charge states which, for heavy elements, are of about 50+ and the charge state distributions are typical of non-equilibrium plasma [4–6].

Interesting information can be given by time-of-flight (TOF) measurements of ions, electrons and clusters in terms of velocity, energy, current and angular distribution. Such investigations indicate the presence of a high electrical field inside the plasma which accelerate ions in the direction of the normal to the irradiated surface [7,8]. Other techniques can be also used to measure the energy of the particles ejected from the hot plasma, such as magnetic and electric deflectors, Wien filters, mass quadrupole spectrometers. Electrostatic deflectors are often employed in order to detect on line the ions emitted from the plasma, and to measure their energy-to-charge ratio. Results of such experiments indicate that the particles have Boltzmann distributions which are shifted toward higher energy for increasing ion charge states [9]. A good test of ion energy measurements is off line analysis of a depth of ion implantation into a given substrate. Such surface analysis may give also interesting

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information about the nature of the ion acceleration processes. In this work, Rutherford backscattering spectrometry (RBS) and Auger electron spectroscopy (AES) were employed to investigate the efficiency of implantation of laser-produced Cu ions into aluminum and silicon substrates.

Plasmas produced by pulsed energetic lasers, in facts, find many applications in different scientific fields. Medicine, physics, chemistry, engineering represent some of these fields. A special interest is devoted to the use of the energetic ions emitted from the laser-produced plasma to induce ion implantation in exposed substrates. Although the ion emission from the plasma is multi-energetic, at high dose the implantation may change significantly the chemical and physical surface properties of many materials. This effect may produce changes in the mechanical properties of the material surface (e.g. hardness, wetting, friction, . . .), in the optical properties (e.g. transmission, absorption, . . .), in the electrical conductibility (especially for polymers) and in the chemical response (e.g. surface reactivity, surface passivation, . . .).

2. Experimental

The implantation experiment has been performed at the PALS Research Center in Prague (Czech Republic). Here, an iodine laser Prague Asterix Laser System (PALS) emits a fundamental wavelength of 1315 nm or its third harmonic of 438 nm. In this experiment, we have used the third harmonic. The duration of the laser pulse is 400 ps and the used laser pulse energy (E_L) was changed in the range 180–230 J. The laser beam was focused on the planar surface of the copper target placed in the vacuum chamber (10^{-6} mbar). The incidence angle of the laser beam is 30°. The focal length of focusing lens was 600 mm and the minimum laser spot diameter was 70 μm. In such conditions the laser fluence was of about 6×10^6 J/cm^2 and the power density of about 1.5×10^{16} W/cm^2. A pure copper flat targets with a surface of 2 cm^2 and 3 mm thickness was irradiated with single laser shots. The measurements of ion energy distributions and ion charge states have been performed by an electrostatic ion energy analyzer (IEA). The IEA contains a cylindrical electrostatic deflector and an electron multiplier (WEM) placed just behind the deflector plates. Fig. 1a shows a scheme of the IEA.

Only the ions with a particular energy-to-charge ratio can be filtered through the deflector and reach the WEM detector. In this way, it is possible to know the charge states, the velocities and the kinetic energy of the Cu ions. More details about the electrostatic ion energy analyzer are given in literature [10].

Different aluminum and silicon substrates exposed to the Cu ions were placed at different distances d from the target and at different angles ϕ with respect to the normal to the target surface.

Rutherford backscattering spectrometry using 1.5 MeV helium beam backscattering at an angle of 165° was employed to investigate substrates implanted and/or deposited with the Cu ions. RBS analyses were performed with the use of Van de Graaf accelerator of the Physics Department of Catania University (Italy). RBS spectra were analyzed using the program RUMP and SRIM of Ziegler et al. [11].

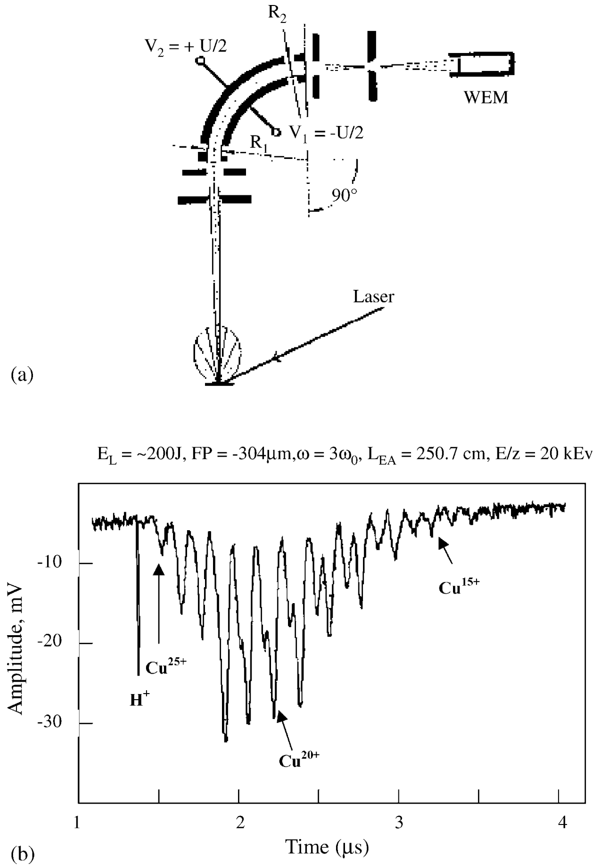

Fig. 1. Schematic view of the ion energy analyzer (IEA) (a) and typical TOF spectrum of Cu ions obtained with the use of IEA at ion energy to charge state ratio E/z = 20 keV (E_L = 200 J) (b).

Auger electron spectroscopy using 3 keV electron beam was employed to study the surface composition of implanted substrates. The AES deep profiles were obtained with a 1 keV Ar sputter gun. AES analyses were performed at the ST-Microelectronics, Physics Lab. M5 of Catania, Italy.

Scanning electron microscopy with associated X-ray microprobe was employed to investigate the morphology of the implanted substrate surfaces.

3. Results

Fig. 1b shows a typical IEA spectrum of the Cu ions emitted normally to the target surface irradiated with the use of the PALS laser system at 438 nm wavelengths with 200 J pulse energy. The spectrum shows the ions detected with a ion energy to charge state ratio of 20 keV/z. Ions with a maximum charge state of 27+ were produced. At this charge state the corresponding ion energy was 540 keV [12]. The charge states of Cu ions increase with the laser pulse energy and intensity determined by the focus position FP with regard to the target surface. The maximum ion charge states at 200 J laser pulse energy was obtained at the laser focus position of about 300 μm in front of the target surface.

Fig. 2 shows three typical RBS spectra related to Cu implantation in Si and Al substrates using 10 laser shots of ~200 J pulse energy, hitting fresh Cu surface. The first spectrum (a) is related to a Si substrate placed at distance $d = 20$ cm from the target and at an angle $\phi = 20^\circ$ with respect to the normal to the target surface. The second spectrum (b) is related to a Si substrate placed also at distance $d = 20$ cm but at an angle $\phi = 30^\circ$. The third spectrum (c) is related to an Al substrate placed at distance $d = 35$ cm and at angle $\phi = 15^\circ$. The upper scale energy reported in each spectrum represents the detected energy of the backscattered alpha particles coming from the surface of the analyzed sample. Such energy scale, depending on the kinematics factor and alpha energy stopping power in the sample surface, permits to correlate the RBS spectrum with the sample depth and to localize the implanted ions with about 20 nm depth resolution [13].

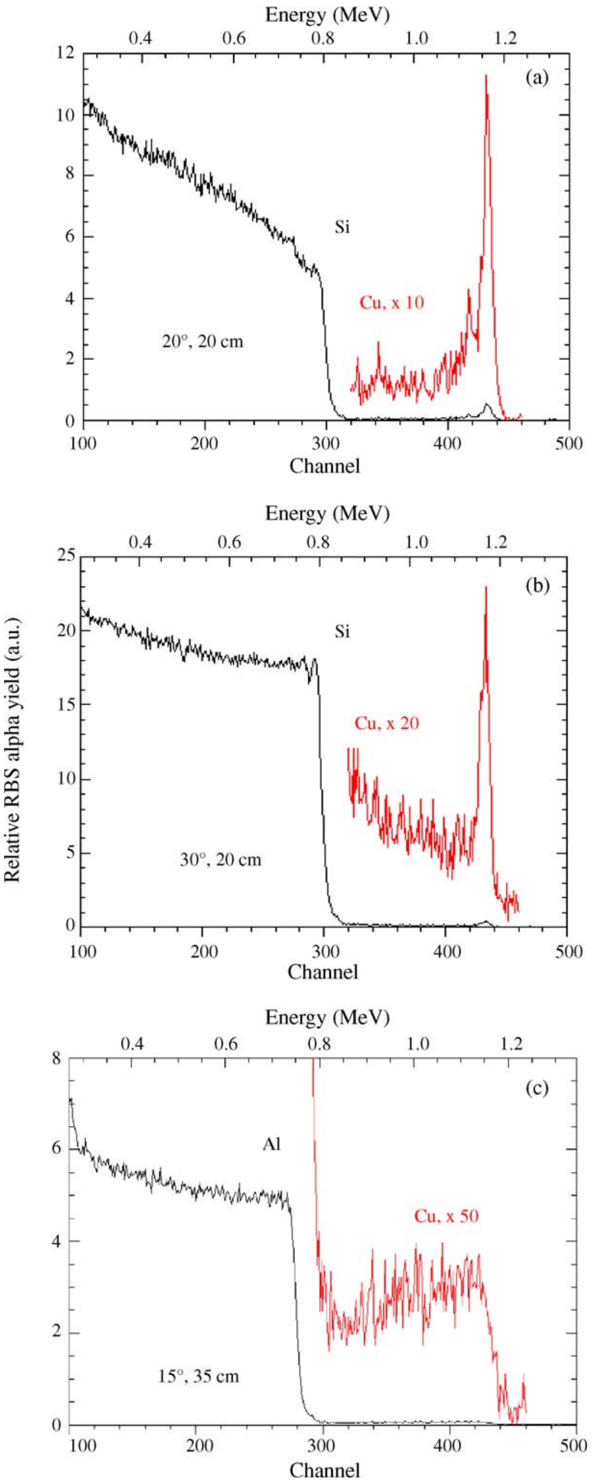

Fig. 2. Comparison of three RBS spectra (1.5 MeV He, 165°) of Cu ions implanted in Si substrates (a and b) and in Al substrates (c) placed at 20°, 20 cm (a), 30°, 20 cm (b) and 15°, 35 cm (c), respectively. The shape of the Cu peaks (base width) is typical of implanted atoms.

The implanted ions have a Boltzmann ion energy distribution depending on their charge state [9]. Thus their range is not well defined such as in the case of mono-energetic ion beams. The depth profile analysis based on the RBS spectra indicate that the Cu ions are implanted at different depths up to about 200 nm, 50 nm and 6000 nm in the three case shown in Fig. 2a–c, respectively. Such RBS experimental data correspond to maximum energies of implanted ions: 270 keV, 60 keV and 850 keV (estimated on the basis of the dependence of the ion penetration depth on ion energy) for these three cases, respectively. The results of the quantitative analysis indicate that the number of implanted Cu ions amounts to 1.8×10^{15} cm^{-2}, 7.5×10^{14} cm^{-2} and 3×10^{15} cm^{-2} for the first, second and third case, respectively.

Fig. 3 shows three RBS spectra of implanted Cu ions in silicon substrates placed at angles $\phi = 30^\circ$ and at distances $d = 15$ cm (a), 18 cm (b) and 50 cm (c) from the target. These, and other experimental RBS results obtained in this investigation, show that the average implanted dose, D, depends strongly on the angle ϕ with respect to the target normal at which the implanted sample is placed. The laser pulse parameters were the same as for Fig. 2. The implanted doses were: 1.8×10^{15} cm^{-2}, 9×10^{14} cm^{-2} and 9×10^{13} cm^{-2} for these three cases, respectively.

Such dependence, in agreement with the literature [14], is well described by the following relationship:

$$D = D_o \cos^6 \phi$$

where D_o is the dose of ions implanted in substrate located at a chosen distance in direction of normal to the target surface. Fig. 4a presents a plot of the implanted dose as a function of angle ϕ for a constant distance $d = 20$ cm.

Of course, the implanted dose depends also on the target–substrate distance. Our experimental data indicate an inverse square dependence of the dose of implanted ions on a substrate–target distance:

$$D = \frac{D_o}{d^2}.$$

Fig. 4b shows plots of the dose of implanted Cu ions as a function of the substrate–target distance d for a fixed angle of 30°.

The surfaces of the implanted substrates were investigated also with the use of SEM and AES methods in order to have better information about their modification as a result of exposition to the ablative plasma plume.

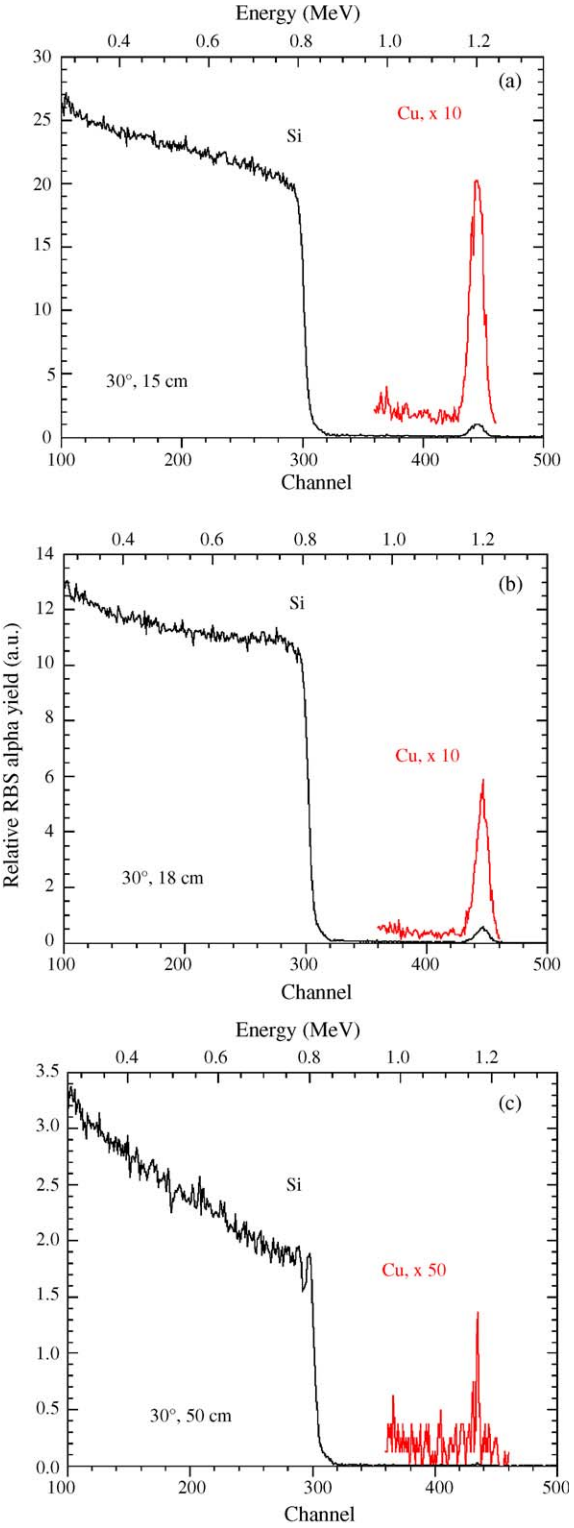

Fig. 3. Comparison of three RBS spectra (1.5 MeV He, 165°) of Cu ions implanted in silicon substrates placed at 30° and at different distances of 15 cm (a), 18 cm (b) and 50 cm (c). The shape of the Cu peaks (narrow peak) is typical of deposited Cu film.

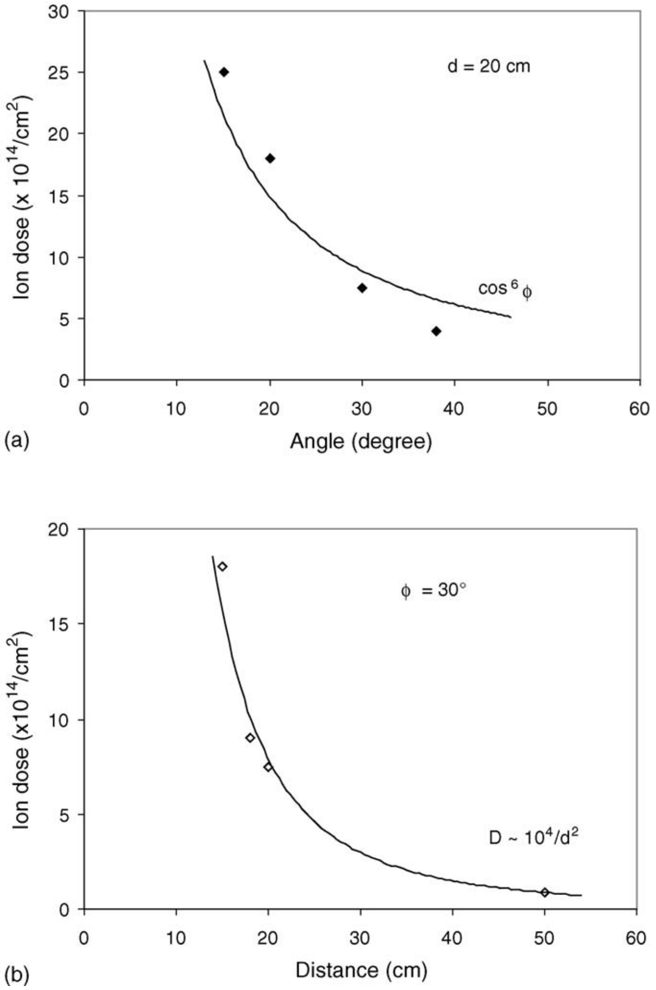

Fig. 4. Dose of implanted Cu ions as a function of the angle with respect to the target normal for substrates placed at the distance of 20 cm from the target (a) and as a function of the distance for substrates placed at an angle of 30° (b).

Fig. 5 presents a typical SEM image of the surface of silicon implanted with Cu ions (a) and a zoom of some sub-micrometric Cu particles detected on this surface (b). The X-ray microprobe analysis detecting the characteristic X-ray fluorescence lines of the elements, performed in the sample zone indicated with ‘1●’, demonstrated that the sub-micrometric particles are due to large Cu clusters, emitting Kα lines at 8 keV (c), deposited on the silicon substrate, emitting Kα lines at 1.7 keV (d).

Fig. 6 shows a typical AES spectrum of the surface of the implanted Si substrate (a) and a typical depth profile of the Cu ions implanted into this substrate (b). AES analysis, at 3 keV primary electrons, demonstrated that the surface contains the Auger characteristic peaks of Cu (LMM = 920 eV) and Si (KLL = 1619 eV). Moreover, the spectra demonstrate that some times the surface contains monolayers of chlorine, carbon, silver, oxygen and aluminum as contaminants due to previous experiment of laser ablation of different metallic targets. The sputtering profiles presented in Fig. 6b, obtained using 1 keV Ar ions, is related to the Cu ions implanted at an angle $\phi = 30°$ and at a distance $d = 20$ cm. Because the sputtering yield measured in silicon is 1 Å/s, the AES profile indicates a Cu penetration depth in silicon of 500 Å, in good agreement with RBS measurements.

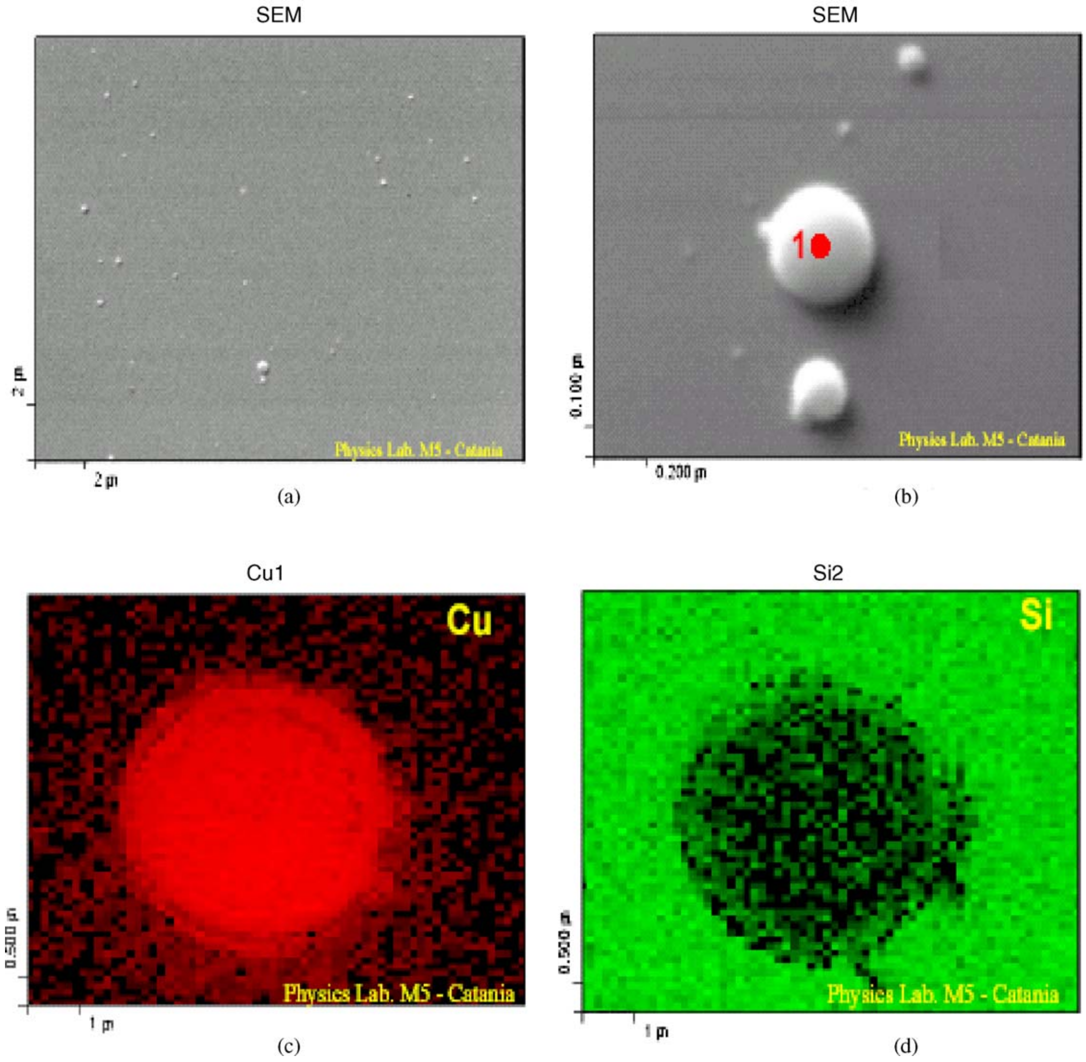

Fig. 5. SEM pictures of a silicon substrate implanted with a Cu dose of about 10^{15} cm^{-2} (a), zoom of sub-micrometric particles deposited on the substrate surface (b), X-ray fluorescence from the copper covering the substrate surface (analysis in the zone '1●') (c) and from silicon in the zone around to the sub-micrometric particle (d).

4. Discussion and conclusions

The ion implantation is the process of exposing a surface to high energy ions which travel some distance (tens to hundreds of nanometers) below the surface before they come to rest. Thus, the implanted ions are an integral part of the surface and not a coating on top of it. This process can dramatically change the physical and chemical properties of the irradiated surface. For example, it changes the hardness, the electrical conductivity, the wear resistance and the chemical reactivity of the surface [15,16]. The changes intensity depends on the implanted dose. Polymers are strongly modified by ion doses of the order of 10^{14} cm^{-2} while metals needs of doses of the order of 10^{17} cm^{-2}. Semiconductors, such as silicon, show significant optical and electrical modifications for implanted doses of the order of 10^{15} cm^{-2}.

The surface modifications concern depth layers depending on the ion penetration depth. Traditionally ion implantation is employed by using mono-energetic ion beams implanted several times at different ion energy to overcome the different depth profiles in order to change the properties of the first superficial layers.

The laser ion implantation is quite simple and very useful for this aim. It accelerates ions at different energy (multi-energetic beam) and may induce implantation at different depth in the substrate. Controlling the ion dose from the number of laser shot and positioning the substrates ad different distances and/or angles with respect to the target normal it is possible to modify the substrate surface properties.

For industrial applications however, a better control of the implanted dose can be obtained by using laser with much lower intensities (~10^{12} W/cm^2) but higher repetition rate (~30 Hz) can be employed. These lasers are less expensive and produce much lower ion energies and much lower charge states. To obtain the needed depth of implantation, the ion energies are increased though electrostatic acceleration, with the amount of acceleration being determined by the product of the charge of the ion and the accelerating voltage. Thus accelerating voltage

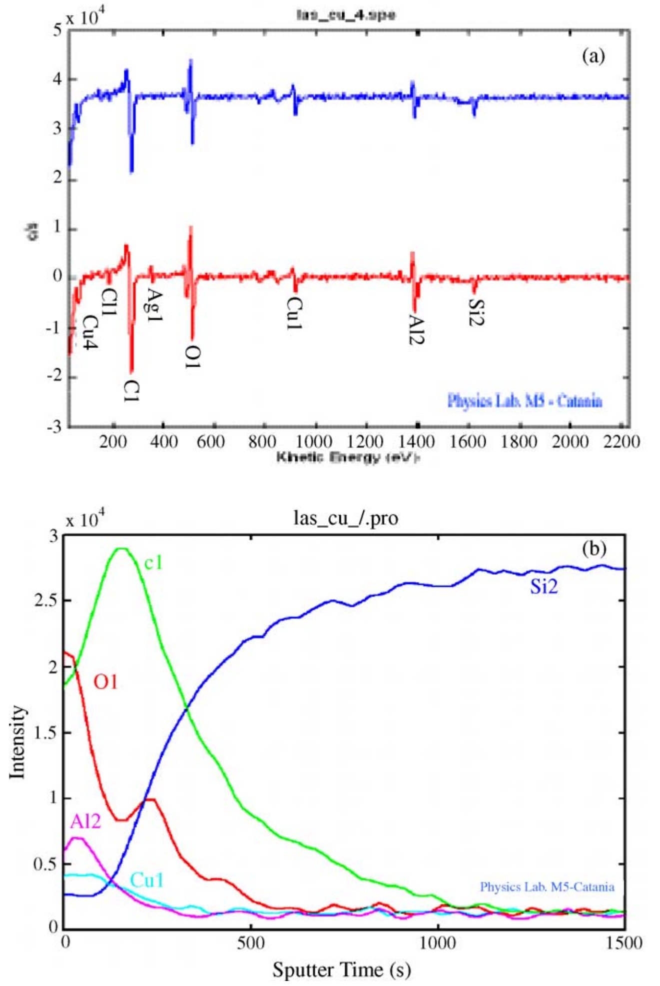

Fig. 6. Two typical AES spectra of the Cu implanted in the Si substrate showing the presence of Cl, C, O, Ag and Al impurities (a) and relative depth profile of the detected elements (b). The Ar-induced sputtering velocity was 1 Å/s.

of 50 kV produces energies of 50 keV for singly charged ions, 100 keV for 2+ charged ions and 250 keV for 5+ charged ions.

The results presented in this work show that the direct ion implantation is successfully obtained using the multi-energetic Cu ions emitted by the hot and dense plasma produced by the PALS laser system. From the off line elaboration of RBS and AES results it was possible to determine the exact Cu ion doses implanted in silicon and in aluminum substrates. Such analysis shows that the angular distributions of ion emission from the laser-produced plasma is very narrow and is centered around the normal to the target surface within the cone angle of about ±30°. The measurements at large angles demonstrate that Cu ions were not implanted and that only a thin film of Cu was deposited on the substrate surface, according to the literature [12].

The plasma ablation, besides ions, electrons, neutrals and molecules, produces small and large clusters as result of splashing processes occurring on the ablated surface at high laser fluency, in good agreement with the literature data [17,18]. These clusters were deposited on the substrate surface, as shows the SEM analysis.

The ion implantations at the PALS laboratory have been performed without any post acceleration and/or focalization of laser-produced ions. The use of electrical and magnetic field located near the target surface may be used in order to have a better control of the ion dose implanted in the substrate at lower laser intensities. Moreover, their use can be employed to select the ion species or to implant only the most energetic ions without introduce in the surface electrons, neutrals, clusters and other contaminants. The authors of this paper are investigating these questions within the Italian INFN project called Plasma Laser Ablation for Ion Acceleration (PLAIA).

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