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Synthesis of Cu/Cr Multilayer Thin Films Deposited by Unbalanced Magnetron Sputtering

Saulius BURINSKAS, Julius DUDONIS

Department of Physics, Kaunas University of Technology, Studentų 50, LT-51368, Kaunas, Lithuania

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Structure and properties of multilayer Cu/Cr thin films deposited by direct current unbalanced magnetron sputtering were analyzed during this work. The leaked plasma of unbalanced magnetron is strongly confined also to the sample holder region, therefore the sample was exposed to ion and electron bombardment, that can lead to intermixing of layers and metastable Cu-Cr alloy formation. The Scanning Electron Microscope images of sample cross-section showed separate Cu and Cr layers, but Cu peak shift in X-ray diffraction pattern indicates that some Cr atoms are dissolved in Cu layer. Resistance measurement during annealing showed that 10 nm Cr layer on Cu is continuous and protects copper from oxidation in temperatures up to 470 °C.

Keywords: Cu/Cr, copper, chromium, multilayer, unbalanced, magnetron, sputtering.

INTRODUCTION

Currently predominant Al-based alloys cannot meet the new requirements for interconnections of nanometer scale microelectronic devices. Copper with its high conductivity has apparent advantages as an interconnection material. However, Cu is quickly oxidized in temperature higher than 100 °C – 150 °C, what can happen in various manufacturing processes. Cu is also known to be a fast diffuser and lifetime killer in silicon. Therefore, multilayer structures are required to prevent interdiffusion and oxidation of copper [1].

Chromium is a good candidate for protecting film due its ability to form thin and dense oxide layer, preventing further oxidation. Also it can be used as a glue layer between the Cu film and the SiO_2 substrate. The adhesion between SiO and Cr is caused by breaking an O–Si bond and forming a Cr–O bond. The adhesion between Cu and Cr is generated by metallic bonding between them, and enhanced by Cu diffusion through Cr grain boundaries. The latter phenomenon, however, may deteriorate the adhesion between Cr and SiO as well as the electrical conductivity of the film, so chromium under-layer must be thicker than the Cu diffusion length in the Cr grain boundaries (~ 8 nm) [2].

Cu–Cr system exhibits a very limited equilibrium mutual solubility which amounts to 0.8 at.% Cr in fcc-Cu at the eutectic melting temperature of 1075 °C, whereas the solubility of Cu in bcc-Cr is negligible, indicating that the heats of mixing in both phases are rather positive. Despite this fact, it was shown that Cu–Cr solid solutions can be obtained by vapor deposition onto cold substrates over almost the entire concentration range, where a transition from an fcc to a bcc structure was observed in the composition range from 29 at.% to 34 at.% Cr for sputtering, and from 30 at.% to 40 at.% Cr for samples prepared by electron beam evaporation [3].

Magnetron sputtering is widely used for deposition of multilayer thin films. In a type-2 unbalanced magnetron the outer ring of magnets is strengthened relative to the central pole. In this case, not all the field lines are closed between the central and outer poles in the magnetron, but some are directed towards the substrate, so the plasma is no longer strongly confined to the target region, but is also allowed to flow out towards the substrate. This leaked plasma then creates a self-bias on the surface of an insulating or isolated film surface. Substrate can become self-biased to up to –30 V, thus high ion currents can be extracted from the plasma without the need to externally bias the substrate [4, 5]. As a result, unlike in other ion-plating processes, the ion-to-atom arrival ratio at the substrate remains constant with increasing deposition rate, what helps to achieve dense film structure [6].

While higher energy ion (>300 eV) irradiation can cause intermixing of layers and in the extreme case degradation of the superlattice structure, low energy (25 eV – 300 eV) ion bombardment during growth has been shown to increase the sharpness of the multilayer interfaces minimizing a combination of interfacial roughness Although the precise mechanism for these structural changes is still under investigation, increased surface adatom mobility and collision induced effects are thought to play an important role [7, 8].

There is not enough information about ion-assisted deposition of multilayer Copper – Chromium thin films, therefore, the purpose of the present investigation is to analyze structure and properties of Cu/Cr multilayer thin films deposited by direct current unbalanced magnetron sputtering.

EXPERIMENTAL PROCEDURE

Multilayer Cu/Cr thin films were deposited by direct current unbalanced magnetron sputtering on the room-temperature crystalline Si substrate for XRD and SEM analysis. Single 20 nm Cu layer and 20 nm Cu – 10 nm Cr bilayer were deposited on oxidized Si substrates with deposited thick chromium contacts for resistance measurement and glass substrates for optical characterization.

*Corresponding author. Tel.: +370-687-75560; fax: +370-37-350737.
E-mail address: *saulius.burinskas@stud.ktu.lt* (S. Burinskas)

Before the deposition, the substrates were ultrasonically cleaned in pure acetone. A vacuum chamber was evacuated by rotary and diffusion pumps to the pressure of $1·10^{-2}$ Pa. Working pressure was kept constant at $2.0·10^{-1}$ Pa by adjusting argon gas flow. Substrate holder was moved in a circular trajectory at 6 cm distance over the planar magnetron target. The rotation speed of sample holder and each magnetron discharge currents were adjusted to achieve required monolayer thickness. Deposition was performed with a constant discharge current density of 25 mA/cm^2 for copper and 37 mA/cm^2 for chromium. The current density from plasma of the unbalanced magnetron to substrate was around –3.5 mA/cm^2. The deposition speed measured with Inficon XTM/2 quartz crystal deposition monitor was 13 nm/s for Cu and 7 nm/s for Cr. The samples were kept in vacuum for 20 min. after deposition to cool down.

The cross-section of multilayer film was analyzed by Scanning Electron Microscope FEI Quanta 200F in secondary electron mode. The crystallographic structure was investigated by X-ray diffraction (XRD) using DRON-UM1 diffractometer and monochromatic Cu Kα radiation. The electrical resistance during annealing in air atmosphere was measured with two-point probe method. The optical transmittance was analyzed with a spectrophotometer ЛОМО СФ-26.

RESULTS AND DISCUSSION

The Scanning Electron Microscope images of Cu/Cr multilayer film cross-section are shown in Figure 1. Secondary electron SEM image seen here is has small sensitivity to Z-number contrast [9]. Pure Cu and Cr also have small difference in electron work functions (respectively 4.8 eV and 4.5 eV) [10]. Despite this fact, we can clearly distinguish copper layers (darker regions) and chromium layers (brighter regions). Since the break of the sample was performed outside the SEM chamber just before measurement, the reason for contrast might be different oxidation capabilities of Cu and Cr as well. Since Cr oxidizes quicker than Cu, the secondary electron yield from its surface can be up to 10 times bigger. Also since breaking the sample was performed without cooling it in liquid nitrogen and Young's modulus and Vickers hardness are respectively 2.3 and 2.9 times bigger for chromium, the contrast reason may by different crack relief in Cu and Cr layers.

It can be seen in Figures 1 and 2, that the layers have some waviness, but are completely continuous. The waviness can be caused by difference in adhesion between layers in some places and different thermal expansion coefficients of metals.

Measurements of layer thicknesses from SEM images were averaged over 440 nm and 1760 nm long segments of layers. The averaged result is 10 nm for chromium and 27 nm for copper. Small disagreement of these result with the prediction based on quartz crystal deposition monitor results (respectively 8 nm and 30 nm) can be addressed to the error caused by sample tilting effect.

Figure 3 shows results of XRD analysis of 1.2 μm thickness film produced on the Si substrate, with the bilayer of 30 nm Cu and 8 nm Cr. The diffraction peaks indicate that the multilayer system consists of <111> textured fcc Cu and <110> textured bcc Cr grains, what is typical for thin Cu and Cr films [10, 11]. To obtain exact position of overlapped Cu (111) and Cr (110) peaks, deconvolution operation was made using pseudo-Voigt function (Fig. 4).

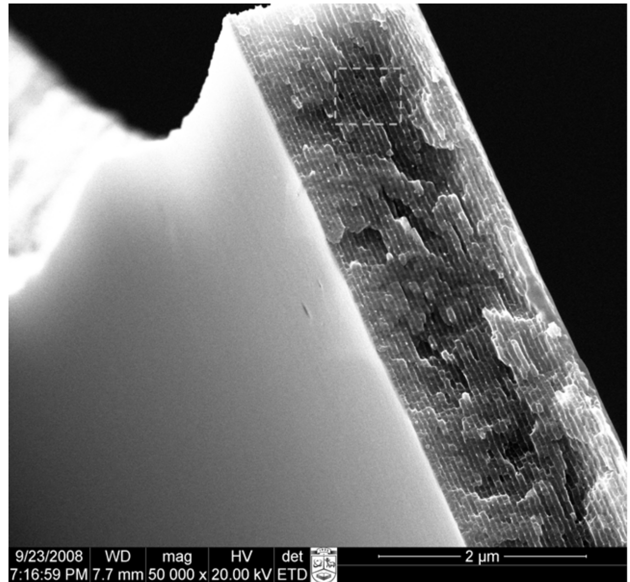

Fig. 1. SEM image of Cu/Cr multilayer film cross-section with magnification 50 000

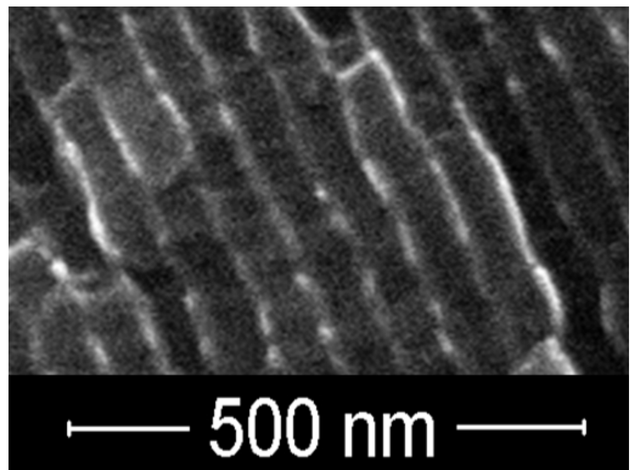

Fig. 2. SEM image of Cu/Cr multilayer film cross-section (digitally magnified from the marked region in Fig. 1)

While the Cr (110) peak in obtained XRD pattern fits to the etalon position, Cu (111) peak is shifted to the position similar to that is observed in Cu-Cr alloy with copper amount between 63 % and 69 % [3]. Since ion-mixing process isn't expected during the unbalanced magnetron deposition and the thickness of Cu layer is bigger than Cr diffusion length at room temperature, the reasons for enhanced Cr diffusion during deposition to Cu layer can be radiation enhanced diffusion. Since the argon ion bombardment during the deposition creates vacancies, the diffusion coefficient can be increased several times. Also bombardment of ions and electrons could heat the upper sample layers to temperatures up to 200 °C and more, what also can enhance diffusion. The third reason for the enhanced diffusion is thermal stresses, caused by

mismatch of thermal expansion coefficients of Cu and Cr metals ($\alpha_{Cu} : \alpha_{Cr} = 16.5 : 4.9$).

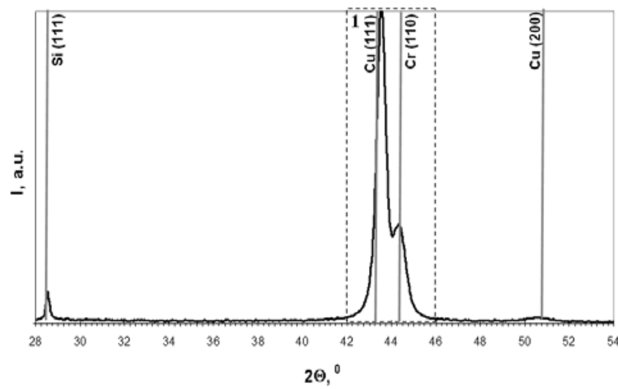

Fig. 3. XRD pattern of Cr/Cu multilayer film produced on the Si substrate

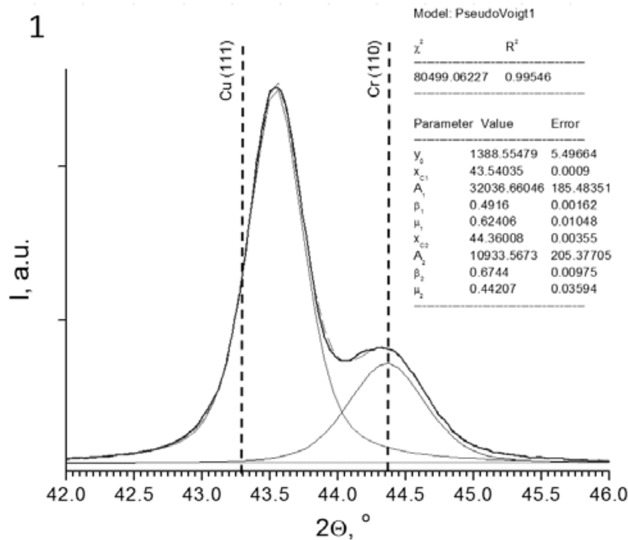

Fig. 4. XRD pattern of Cr/Cu multilayer film after Cu(111) and Cr(110) peak deconvolution

The lattice constants calculated according to Bragg's law are $a_{Cr} = 0.289$ nm and $a_{Cu} = 0.360$ nm. The decrease is less than 1 % comparing to the lattice etalons (0.291 nm and 0.361 nm respectively) [12]. The lattice constant increase was expected, but the influence of compressive stress in film was stronger than cell changes due to incorporation of different size atoms.

Crystallite size was calculated with Scherrer equation using FWHM obtained from pseudo-Voigt function parameters: $D_{Cu} = 22$ nm and $D_{Cr} = 15$ nm. The calculated Cr crystallite size is larger than Cr monolayer thickness that can be due to error of Scherrer method and also due to possible growth of long crystallites of Cr.

To find out temperature range, in which chromium film protects copper from oxidation, 20 nm thickness copper film and bilayer film of 10 nm Cr on 20 nm Cu, both deposited on oxidized Si substrates were annealed in air atmosphere. Resistance measurement during annealing in temperatures from 20 °C to 200 °C showed rapid Cu film oxidation at the 170 °C (Fig. 5), while thin film of 20 nm Cu covered with 10 nm Cr showed no resistance changes. Resistance measurement during annealing at higher temperatures showed Cu/Cr bilayer oxidation only at 470 °C (Fig. 6). These results confirm that 10 nm thickness Cr layer on Cu is continuous.

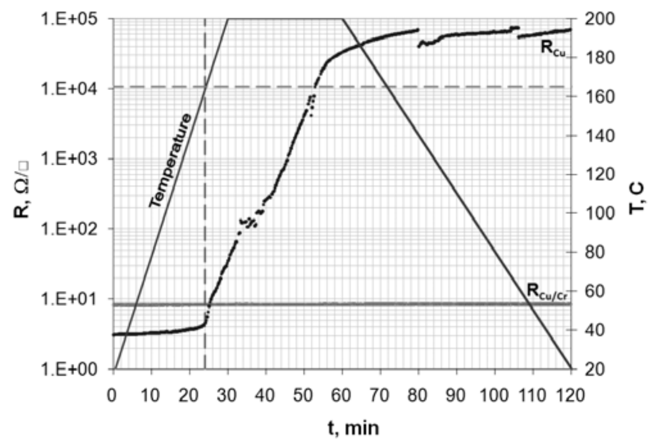

Fig. 5. Results of sheet resistance measurement during annealing Cu and Cu/Cr bilayer film at temperatures up to 200 °C

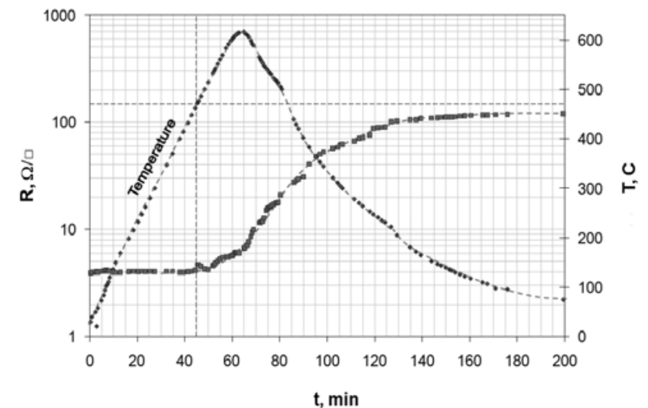

Fig. 6. Results of sheet resistance measurement during annealing Cu/Cr bilayer film at temperatures up to 600 °C

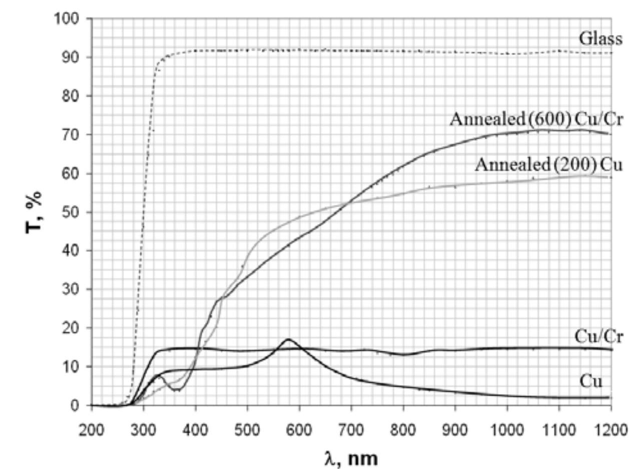

Fig. 7. Optical transmittance spectrum of Cu and Cu/Cr bilayer films produced on the glass substrates

As it can be seen from Fig. 5 and Fig. 6, the final Cu-Cr bilayer sheet resistance (120 Ω/□) is several magnitudes lower than Cu layer after oxidation (71 kΩ/□). It was shown by [1] that at 450 °C temperature rapid Cr diffusion and intermixing with Cu is expected. At 600 °C temperature rapid oxygen diffusion through Cr layer also is

expected, what should cause full Cu layer oxidation. Since the final sheet resistance of Cu/Cr bilayer remained much lower than the oxidized single Cu layer, only partial oxidation of protective Cr layer may be expected at short time annealing at 600 °C.

Optical transmittance measurement confirmed that the samples were strongly oxidized during annealing (Fig. 7). Before annealing spectra of both samples were typical to thin metal film. In the Cu metallic film spectrum we can see characteristic peak at 580 nm which disappears after annealing. It can be seen that the transmittance increased several times after annealing: from ~10 % to ~40 % in visible light wavelength (400 nm – 700 nm) region and to ~60 % in infrared wavelength (700 nm – 1200 nm) region. This is typical behavior for thin film of semiconducting Cu_2O that is more transparent to infrared light than CuO due to wider band gap ($E_{g,Cu20}$ = 2.1 eV and $E_{g,CuO}$ = 1.2 eV with corresponding wavelengths 625 nm and 900 nm) [13].

CONCLUSIONS

SEM and XRD results showed that Cu/Cr multilayer films with 10 nm Cr layers without full intermixing can be deposited by direct current unbalanced magnetron sputtering. SEM cross-section images showed separate Cu and Cr layers. Resistance measurement during annealing in air atmosphere showed that Cr forms continuous layer that protects Cu from oxidation in 20 °C – 450 °C temperatures range. Chromium film protection failed at temperatures higher than 470 °C.

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