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Laser-induced chemical liquid deposition of discontinuous and continuous copper films

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Abstract

ArF and KrF laser photolysis of Cu(II) acetylacetonate in 2-propanol affords chemical liquid deposition of Cu agglomerates on quartz and glass. The process is achieved through interaction of Cu colloids with these surfaces. The films were characterized by UV–Vis spectroscopy, electron microscopy and X-ray photoelectron spectroscopy. Properties of the deposited copper agglomerates differ depending on the irradiation conditions: those produced with KrF laser radiation form continuous films, whereas those obtained with ArF laser radiation are nano-islands containing more Cu oxides in topmost layers.

Keywords: Copper films; Laser photolysis; Cu(II) acetylacetonate; Chemical liquid deposition

1. Introduction

Nano-sized particles and nano-structured continuous and discontinuous films of copper and copper oxides deposited on dielectrics have been intensely studied in recent years.

Fabrication of nano-sized particles [1–4] and thin films [5–7] of copper on dielectrics is of great recent interest due to a wide range of promising properties (non-linear optic effects, high catalytic efficiency and reactivity) and potential use in optical switching devices, catalytical systems, interconnections in microelectronic components and others. Copper nano-particles in insulating matrix have been fabricated using ion implantation [1,8,9], excimer laser irradiation of an organometallic compound crystals embedded in polymer matrix [10], atomic layer deposition [2] and by heating of Cu^{II}-doped dielectrics [3,4]. Copper films on dielectric substrates have been obtained by chemical vapor [11–16], laser chemical vapor [17] and reactive vapor [18] deposition and RF and DC magnetron sputtering [5,6,19,20].

Nano-sized particles and nano-structured films of cuprous and cupric oxide have potential application in solar and photoelectrochemical cells, catalysis and sensors (e.g. [21]). Nano-structured Cu_2O films on dielectrics were prepared by electrochemical deposition [22] and nano-sized crystalline Cu_2O particles were obtained by physical (evaporation–deposition [23], cryo-melting [24]) processes, reduction in solution (e.g. [25–27]), electrochemical route [28] and solution chemistry assisted by γ- [29] and microwave [30] radiation. Nanocrystalline CuO films on quartz were prepared by pyrolysis of Cu-arachidate [31] and CuO nano-particles on dielectrics were obtained by controlled oxidation of Cu nano-particles within silica gels [32]. The latter were also produced by precipitation [33], spin coating [34], solid-state [35] and sonochemical [36] reaction and solvothermal [37] and electrochemical [38] routes.

The growth of Cu_2O nano-islands on dielectrics has been accomplished by oxygen-plasma-assisted molecular beam epitaxy [39] and metalloorganic chemical vapor deposition [40,41].

In this paper we continue our previous activity on laser photolytic-chemical liquid phase deposition (e.g. [42–44]) and describe the first photolytic formation of nano-structured Cu

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films on dielectrics by using excimer laser-induced chemical liquid-phase photolysis of copper(II) acetylacetone) in alcohol. This laser-induced, clean process takes place in the absence of reducing reagents through interaction of photolytically produced Cu sols with surface and makes possible large area deposition.

2. Experimental

Laser-assisted deposition of Cu films in the liquid phase was examined in a simple set-up. Briefly, samples of Cu(II) acetylacetonate (Aldrich, 50 ml of 1.5×10^{-3} M solutions in 2-propanol (Cica-reagent for spectroscopy)), were photolysed in a Pyrex vessel (ca 70 ml in volume) equipped with a demountable (1 × 2.5 cm) quartz window and two valves for connection to an Ar gas supply and a vacuum line (Fig. 1). The solutions were de-aerated by using vacuum (three freeze–thaw cycles), bubbled with Ar and irradiated with an LPX- 200 (Lambda Physik) laser under argon. The solutions stirred by a magnetic bar were exposed to ArF laser radiation at 193 nm and KrF laser radiation at 248 nm with a repetition frequency of 10 Hz delivering respective energy of 130 and 650 mJ per pulse (measured by a Gentec ED-500 joulmeter). The laser beam was incident to the whole surface of the reaction window. The incident fluence delivered with the ArF laser non-focused radiation was 30 mJ cm^{-2} and that delivered with the KrF laser mildly focused irradiation was 540 mJ/cm^2. The ArF and KrF laser photolysis of Cu(II) acetylacetonate lasted 10 and 30 min, respectively. As a result of these different conditions, deposition of copper coatings on the whole surface of the entrance window in the former case, or deposition of copper coatings on the whole reactor surface (and on immersed added quartz and glass plates (ca. 1 cm^2)) in contact with the solution in the latter case was accomplished. After the irradiation ceased, the irradiated solution was removed and the entrance window and the substrate coated with the films were detached from the Pyrex vessel, rinsed with the de-ionized water and dried under argon.

The deposited films, as grown on the substrates, were examined with UV spectroscopy, electron microscopy and photoelectron spectroscopy.

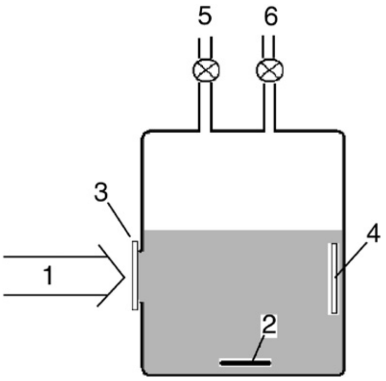

Fig. 1. Vessel for laser-photolytic decomposition of copper(II) acetylacetonate. 1, laser beam; 2, stirring bar; 3, quartz window; 4 glass substrate; 5, vacuum; 6; Ar gas supply.

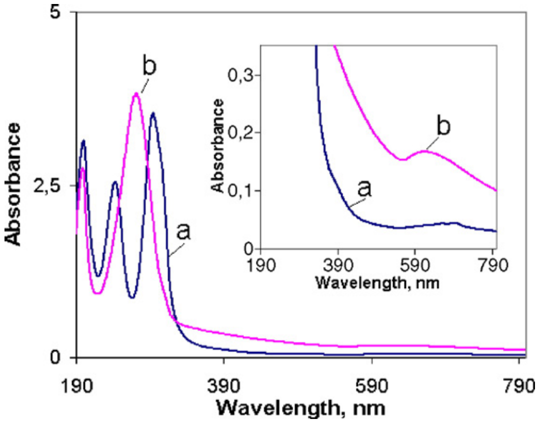

Fig. 2. Absorption spectra of Cu(II) acetylacetonate (1.5×10^{-3} M solutions in 2-propanol) diluted in hexane before (a) and after (b) irradiation with ArF laser.

The photolytic progress on the irradiated samples (0.5 ml) diluted with hexane (Cica-reagent for spectroscopy, 3 ml) was monitored by UV–VIS spectrometry (a Shimadzu UV-2450 UV–VIS spectrometer) in the 4 ml quartz cells.

The centrifuged solutions freed from Cu agglomerates were analyzed on a Shimadzu QP5050 gas chromatograph-mass spectrometer (60 m long capillary column with Neutrabond-1 as a stationary phase, programmed temperature 30–200 °C).

SEM images were acquired using a Philips XL30 CP scanning electron microscope equipped with energy-dispersive analyzer (EDAX DX-4) of X-ray radiation. A PV 9760/77 detector in low vacuum mode (0.5 mbar, voltage 5 kV) was used for determination of C, Cu, O and Si content. TEM analysis (particle size and phase analysis) was carried out on a Philips 201 transmission electron microscope at 80 kV on deposited materials scraped from quartz and glass surface. Process diffraction [45] was used to evaluate and compare measured electron diffraction patterns with an XRD diffraction database [46].

X-ray photoelectron spectra were measured on VG ESCA 3 MkII electron spectrometer using Al Kα radiation (hv = 1486.6 eV) for excitation. Detailed scans were taken over Cu 2p, Si 2p, C 1s and O 1s spectral regions. In addition, the spectra of Cu $L_3M_{45}M_{45}$ Auger electrons excited by X-ray radiation were measured. The pressure of residual gases during spectra acquisition was typically 10^{-7} Pa. The peak positions and areas were determined by fitting the unsmoothed spectra after subtraction of linear background. Curve fitting of overlapping spectral lines was carried out using the lines of Gaussian–Lorentzian shape and using XPSPEAK 4.1 fitting software [47]. Theoretical photoionization cross-sections [48] were used to convert peak intensities into the elemental concentrations [49].

3. Results and discussion

UV absorption spectrum of copper(II) acetylacetonate consists [50,51] of bands at 280–310 nm, 230–255 nm and 190–210 nm. The second and third band located at the emission wavelength of the KrF (248 nm) and ArF (193 nm) laser respectively correspond to a charge–transfer transition of the