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Optical and structural properties of copper nanostructured thin films prepared by pulsed laser deposition

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ABSTRACT

In this paper, preparation of nanostructured copper thin films using the pulsed laser deposition technique has been described. Thin films have been prepared at high vacuum, which assures impact of highly energetic ablated species on the film surface. Role of deposition time variations on changing the films nanostructure has been studied and it is shown that by increasing the deposition time, it will evolve from isolated nanoparticles into nanoclusters and eventually a percolated structure composed of aggregated nanoparticles. Furthermore, by increasing the deposition time and consequently the volume fraction of copper nanoparticles, a blue-shift in plasmon absorption peak of our nanostructured copper thin films has occurred and the plasmon linewidth has narrowed simultaneously, which is not in accord with the previous reports. Source of this intriguing behavior has been ascribed to the energetic nature of impacting particles on the film surface at high vacuum conditions and the subsurface growth mode which can facilitate the formation of metastable phases.

1. Introduction

In recent years, nanostructured thin films (NTFs) have attracted great attention since the nanostructure plays a pivotal role in determining optical, electrical, magnetic and mechanical properties [1–4]. Due to quantum size effect, physical and chemical properties of these films can be quite different compared with their bulk systems. These NTFs are used in different fields like electronic devices, medicine, and energy production and savings. Thus far, thin films containing various shaped nano-objects, like nanoparticles, nanorods, nanowires, etc. have been investigated.

Copper nanoparticles have attracted wide interest because of their optical, catalytic, mechanical and electrical properties, resulting in a broad range of applications in the field of metallurgy, catalysis, nano- and optoelectronics [5]. Accordingly, a variety of methods have been used for their preparation ranging from wet phase preparations, hydrothermal, sonochemical or chemical reduction to gas phase processes [6–11].

Compared to different chemical and physical deposition techniques, pulsed laser deposition (PLD) has distinct advantages for preparation of NTFs [12,13]. The most dominant advantage of the PLD technique is that the prepared films are almost free of contaminants, since the laser which is used for creation of nano-objects in this technique is a clean source of energy. The laser ablated plasma plume contains large amounts of particles with typical size in the few nanometer range [14,15]. By managing the laser pulse features and deposition geometry, it is possible to control the size of nanoparticles and the resulted nanostructure of thin films. Various controllable parameters, like the laser pulse width and energy, vacuum pressure, target to substrate distance, deposition time and the substrate rotation speed and temperature [16], make this technique a versatile tool for preparation of NTFs.

Growth of metallic films by PLD differs considerably from other deposition methods because of its high instantaneous deposition rates and the high kinetic energy of the deposited species in the hyperthermal energy interval ($\approx$1–10^3 eV) [17,18]. These characteristics result in the subsurface, or subplantation growth mode that differs from the traditional models [19] and the capability of PLD as a means to prepare films far away from thermal equilibrium [20] in metastable phases [21].

In the present work, preparation of copper NTFs using the PLD technique has been described and role of deposition time on optical and structural properties of the prepared films has been investigated.

2. Experimental

Copper NTFs were prepared using the PLD technique. The schematic of our used PLD system is represented in Fig. 1. To this end, a Nd:YAG laser operating at 532 nm and capable of supplying

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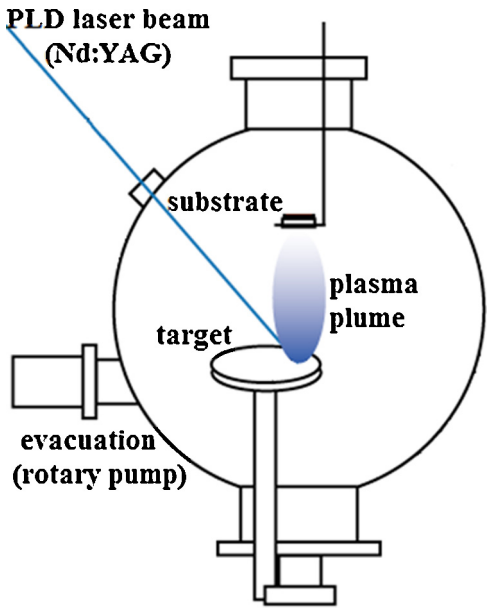

Fig. 1. Schematic illustration of our used PLD system.

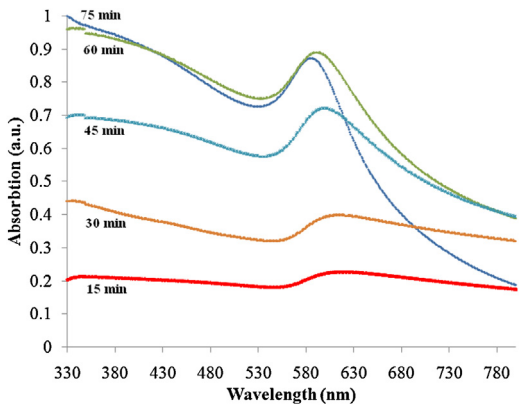

Fig. 2. Optical absorption spectra of the prepared copper NTFs. All the absorption spectra are normalized to the maximum absorption of the film prepared for 75 min.

Table 1
Plasmon absorption peak wavelengths as well as their linewidths for the copper NTFs prepared for different deposition times.

Deposition time (min)	Plasmon resonance wavelength (nm)	FWHM (nm)
15	619 ± 4	121 ± 6
30	614 ± 5	120 ± 3
45	597 ± 2	66 ± 4
60	587 ± 5	52 ± 4
75	583 ± 2	42 ± 3

greater than 40 mJ per pulse (at repletion rate of 10 Hz) with pulse lengths of $\tau = 20$ ns, was focused to give an energy density of $\approx 1.5\,J\,cm^{-2}$ on the target. To reduce the detaching possibility of the unwanted macroscopic species from the target surface, its surface has been carefully polished with emery papers and thereafter, cleaned by ultrasonication in ethanol and deionized water, respectively. The laser beam was irradiated on the target surface at an angle of 45° with respect to its normal and the target to substrate distance was kept constant at 2.5 cm as the optimal distance [22]. The depositions were performed in a chamber with a background pressure of around 200 μTorr. The target holder was rotated at 40 rpm to prevent crater formation in a single location on the target surface and the substrate was rotated at 60 rpm to improve the coating layer uniformity. Three series of samples were prepared for deposition times of 15, 30, 45, 60 and 75 min on glass substrates.

Immediately after removing the films from the deposition chamber, their optical absorption spectra were measured in a spectrometer (Varian Cary 5000) in UV–visible wavelength range. Thin films obtained were characterized by scanning electron microscopy (SEM) and atomic force microscopy (AFM). Using the SEM and AFM data, morphology of the films were studied and surface roughness in the prepared NTFs were measured.

3. Results and discussion

Fig. 2 shows the optical absorption spectra of the prepared copper NTFs. Plasmon absorption peaks are visible on absorption spectra of the films prepared for different deposition times. Presence of plasmon peaks provides clear evidence in support of copper nanoparticles formation on the surface of the films. Looking more closely at Fig. 2 reveals that as the deposition time has increased, the plasmon peak of the copper NTFs has shifted more toward the blue end of the visible spectrum and its width has become narrower. In order to more clearly see these features, the measured wavelengths at which plasmon resonance have occurred for the copper NTFs and their full width at half maximum (FWHM) are listed in Table 1. According to the Mie theory, the wavelength at which plasmon resonance occurs depends on optical characteristics of the medium which surrounds the nanoparticles. In our case, due to the highly energetic nature of the ablated species from the target surface, the copper nanoparticles will grow some monolayers beneath the glass substrate surface [23] during pulsed laser deposition.

For copper nanoparticles inside Al_2O_3 [24] and $Ba_{0.5}Sr_{0.5}TiO_3$ [25] media, plasmon peaks at 590 and 580 nm have been reported, respectively, which are in agreement with the wavelengths given in Table 1 for the copper nanoparticles inside glass. Experimentally, it is also shown that the plasmon wavelength as well as the plasmon linewidth depend on the type of nanostructure created on the film surface [25,26]. Indeed, for the case of copper nanoparticles in $Ba_{0.5}Sr_{0.5}TiO_3$ host material [25], a red-shift in plasmon wavelength has taken place by increasing the volume fraction of copper nanoparticles and at the same time, the plasmon linewidth has broadened.

In Fig. 3, SEM pictures of the copper NTFs are shown. As can be seen, for the films prepared for 15 min, morphology consists of isolated nanoparticles with more or less smooth rounded edges and with typical size in the range of few tens of nanometers. One should bear in mind that in vacuum conditions, controlling the size of deposited nanoparticles is difficult and one cannot obtain a homogenous size distribution. Indeed, it is shown that more uniform size distribution can be obtained by using a background gas during the PLD process [1]. As the deposition time has increased to 45 min, the morphology has changed to nearly separated islands, some of which are elongated. This elongated shape indicates that they result from coalescence of smaller nanoparticles, some of which can still be observed as isolated nanoparticles on the film surface. Turning to the surface of the film prepared for 75 min (Fig. 3c), since the number of arrived nanoparticles on the surface has further increased, a percolated structure is formed by the aggregation of small nanoparticles.

AFM images of the copper NTFs are shown in Fig. 4. By inspecting this figure one can observe that as the deposition time increases from 15 to 75 min, the surface coverage also increases and isolated nanoparticles coalesce together to form a more uniform topology. The measured root mean square (rms) surface roughnesses of the films are given in Table 2. The surface roughness has increased by