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The evolution of Cu_3N films irradiated by femtosecond laser pulses

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ABSTRACT

Copper nitride (Cu_3N) films have been prepared on glass substrates by DC magnetron sputtering in the presence of an Ar + N_2 atmosphere at room temperature. We study the surface chemicals and structures of Cu_3N films irradiated by tightly focused femtosecond laser pulses in the air. The evolution of microstructure, morphology of Cu_3N films is analyzed by means of X-ray diffraction (XRD), optical microscopy (OM), and scanning electron microscopy (SEM). XRD analyses clearly indicate that Cu phases are formed under femtosecond laser irradiation. Moreover, SEM images show that dispersed particles on the surface tend to form continuous porous films with decrease of laser power density.

1. Introduction

Copper nitride (Cu_3N) as a fascinating nontoxic semiconductor has attracted considerable attention over the last two decades. Cu_3N has a structure of cubic anti-ReO_3 (space group Pm3m), in which the copper atoms occupy the center of the cubic edges and the nitrogen atoms occupy the corners of the cell. Due to its poor thermal stability, Cu_3N decomposes into metallic copper and nitrogen at a quite low temperature (about 100–470 °C) [1–4]. This progress can be induced by heating, ion, electron and laser beam irradiation. The radiation-induced decomposition of Cu_3N opens its possibility usage in write-once optical storage devices with a strong reflectivity contrast, because the optical reflectivity of copper nitride in visible and infrared range is far smaller than that of pure Cu [5,6]. As reported by Nosaka et al. [7], a Cu_3N film could be locally decomposed by electron beam irradiation such that microscopic Cu dot array could be "written" on the Cu_3N. Moreover, it was found that four data tracks were written on a Cu_3N-layer by pulsed diode laser irradiation and the writing data rate was 3.3 Mbits/s, which demonstrated the suitability of Cu_3N for write-once optical storage [8]. Besides, laser process enabled the formation of micrometric conductive Cu-metal dot and line patterns [7] by the decomposition of Cu_3N having a signal speed higher than those based on Al, which could be used in integrated circuits. Catrin et al. [9] researched the laser interference patterning of Cu_3N films by nanosecond pulse Nd:YAG laser. However, to the best of our knowledge, there are no reports on femtosecond pulse laser irradiation of Cu_3N films.

Cu_3N films have been successfully grown by various techniques, such as sputtering [10,11], atomic layer deposition [12,13], chemical vapor deposition [14] and other methods [6,15]. In this work, Cu_3N films were deposited on glass substrates by reactive DC magnetron sputtering of a Cu target at room temperature. The aim of this article is to investigate the route of the decomposition of Cu_3N films irradiated by femtosecond laser. For this purpose, the morphological and microstructural evolutions of Cu_3N films have been characterized prior to and after irradiation in air with various laser power density by X-ray diffraction, optical microscopy and scanning electron microscopy. Meanwhile the electrical resistivity changes of the films were analyzed.

2. Experimental

500 nm thick Cu_3N films were deposited on glass substrates by DC magnetron sputtering using a copper target (99.99%) at room temperature. Working gas was a mixture gas of nitrogen (99.999%) and argon (99.999%) with the ratio of 1:1. Before the film deposition, the sputter chamber was extracted to a vacuum of 8×10^{-4} Pa. The total working gas flow was fixed at 40 sccm (standard cubic centimeter per minute), and the pressure was fixed at 1 Pa. The distance between the substrate and target was about 60 mm with a DC power of 50 W during the sputtering.

The irradiation experiments of Cu_3N films were performed using an amplified Ti: sapphire femtosecond laser system that was operated at a wavelength of 800 nm, with the laser power of 100 mW, the laser pulse duration of 35 fs and the repetition rate of 1 kHz. A

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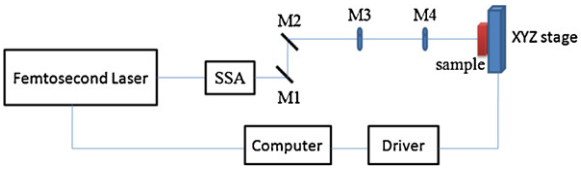

Fig. 1. Schematic diagram of experimental setup for femtosecond laser irradiation of Cu_3N films.

schematic diagram of the experimental setup was shown in Fig. 1. The incident laser was irradiated on the Cu_3N films through single shot autocorrelater (SSA), reflecting mirrors (M1 and M2), circular variable neutral density filter/beamsplitter (M3) and tightly focused lens (M4). A high precision computer-controlled XY-stage (for the sample) and Z-stage (for the objective lens) allowed precise positioning of the spot on surface sample. The laser beam was perpendicular to the sample surface and the spatial profile of the laser pulse was found to be nearly Gaussian. The focal spot size about 55 μm in diameter was obtained with a lens (f = 50 mm). The samples were irradiated to produce scanning patterns by translating the samples relatively to the stationary laser beam along the horizontal direction followed by a vertical shift, and the scanning area of Cu_3N film was 15 mm × 3 mm. The scanning speed was 20 mm/s and the vertical shift step was 0.1 mm. In order to eliminate ablation and analysis the decomposition of Cu_3N film, the beam intensity was reduced by increasing the distance between the sample surface and the focal plane. The distances were 2.5–4.5 mm, and the corresponding laser spot sizes varied from 75 to 131 μm. The Cu_3N samples irradiated on various focal locations were referred as sample 1–5 (as presented in Table 1).

The phase composition and crystalline structure of the samples were verified by X-ray diffraction (CuKα radiation). The surface morphology was measured by optical microscopy (OM), and scanning electron microscopy (SEM). In addition, an optical image analyzer was used to measure spot diameters and the thicknesses of films were measured by a profilometer (DEKTAKII). The sheet resistances of the films were measured with Keithley 2400. Two Ag electrodes were made on the square sheet edges of Cu_3N samples, the gold-plated probes were positioned in Ag electrodes. After selecting a current measuring range which was applied stepwise from −0.1 A to +0.1 A in a step of 0.001 A, and the sheet resistance was calculated using the V/I measurement method.

3. Results and discussion

3.1. Microstructural analysis

Fig. 2 shows the X-ray diffraction patterns of as-deposited Cu_3N film and the samples irradiated by the laser with various power densities. Fig. 3 shows morphological evolution of irradiated Cu_3N films. Fig. 3(a) is photos of samples 1–5 observed by camera. Fig. 3(b)–(f) are amplified images observed by OM corresponding to samples 1–5 in Fig. 3(a), respectively. The as-deposited film exhibits strong Cu_3N (1 0 0), (1 1 1) and very weak Cu_3N (1 1 0), (2 0 0) peaks, which corresponds to cubic anti-ReO_3 structure of

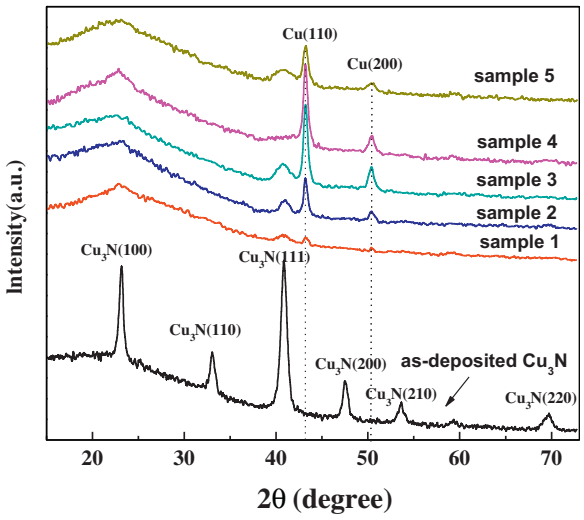

Fig. 2. X-ray diffraction patterns of the as-deposited Cu_3N films and the samples irradiated by femtosecond laser with different laser power densities, referred as samples 1–5.

Cu_3N. Peaks related to pure Cu, or N-compounds are not observed. After irradiation, in XRD pattern of sample 1, Cu_3N peaks disappear and just an extremely weak Cu (1 1 1) peak exhibits, which implies that Cu_3N film is almost directly ablated by femtosecond laser with a high laser power density of 2214 W/cm^2. This result can be also seen from Fig. 3(a), in which the position on the glass substrate corresponding to the laser irradiation on the Cu_3N film is almost transparent. Because Cu_3N films were irradiated by a laser beam with a Gaussian intensity distribution, the laser power density on facular boundary region was relatively small, thereby there existed a residual part which was metallic Cu decomposed from Cu_3N (as shown in Fig. 3(b)). As the laser power density decreases, the peaks corresponding to Cu (1 1 1) and (2 0 0) clearly appear in XRD spectra of samples 2–4 and the intensity of the Cu (1 0 0) diffraction peak is strengthening, which is an evidence showing that Cu_3N is decomposed into copper and nitrogen, and the direct ablation of Cu_3N from the glass substrate is obviously weakened. However, very weak Cu_3N (1 1 1) peak is still observed in samples 1–3, which indicates the films located on the spacing between the scanning lines are not completely decomposed, because laser spots for samples 1–3 are not big enough to cover the whole area of Cu_3N film. The Cu (1 0 0) diffraction peak of sample 5 becomes weak with the decrease of the laser power density, meanwhile Cu_3N appears. This result suggests that laser irradiation with a power density below 741 W/cm^2 can't induce complete decomposition of Cu_3N film. All these data suggest a delicate balance of ablation and decomposition contributions to determine an optimal decomposition rate of the Cu_3N film.

3.2. Morphological evolutions

As shown in Fig. 3(a), different film colors are presented after irradiation. Sample 1 and 2 are almost transparent, sample

Table 1
The power, spot diameter and laser power density of all samples irradiated by femtosecond laser.

Irradiated sample	Power (mW)	Spot diameter (μm)	Laser power density (W/cm^2)
1	100	75	2214
2	100	85	1755
3	100	98	1316
4	100	112	1009
5	100	131	741