Copper nitride and tin nitride thin films for write-once optical recording media

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The feasibility of using copper nitride and tin nitride thin films as write-once optical recording media was explored. The Cu_3N and SnN_x films were obtained by the reactive sputtering method. They were thermally decomposed into Cu and Sn films at 470 and 550 °C, respectively. The Cu film obtained by the thermal decomposition showed a large difference in reflectance which is applicable to the optical recording media. The Sn film obtained by the thermal decomposition included SnO, and consequently it showed a small difference in reflectance from that of SnN_x film. © *1996 American Institute of Physics.* [S0003-6951(96)03833-8]

Write-once read many (WORM) optical storage involves a variety of materials. Among them, tellurium-based thin films are widely used as stable and highly sensitive memory media. However, preparations of the films have suffered from the fact that tellurium itself is toxic and unstable in air.

Copper nitride (Cu_3N) and tin nitride (SnN_x) are nontoxic and stable in air at room temperature, and they change into metals of high reflectivity by thermal decomposition at low decomposition temperatures. Asano *et al.*[1] prepared the Cu_3N films by ion-assisted vapor deposition, and made preliminary experiments of the write-once optical recording on this film. They reported that the Cu_3N film was decomposed into Cu film by heating at 300 °C for 1 h in argon. A previous study by Maya[2] was concerned with another application of these low decomposition temperatures. He obtained the films by dc sputtering, and explored the feasibility of using the coating to generate microscopic metal lines by maskless laser writing. He reported that Cu_3N and SnN_x decomposed into the elements with the rate reaching a maximum at 465 and 615 °C, respectively.

The present study was undertaken to establish the feasibility of utilizing the relatively low thermal stability of Cu_3N and SnN_x to generate metallic reflection by thermal decomposition.

In preparing nitride films, rf (13.5 MHz) magnetron sputtering equipment (Osaka Vacuum, Ltd.) was used with 99.99% pure copper and tin targets of 10 cm in diameter and 1 mm thick.[3,4] The rf power was 50 W. The sputtering gas was a 99.999% pure nitrogen. The separation distance between the substrate and the target was 48 mm. The chamber vacuum just before growth was less than 2.0×10^{-6} Torr. The substrate temperatures were 99 and 86 °C for Cu_3N and SnN_x, respectively. They were measured using a chromel–alumel thermocouple attached to the front of the substrate holder. The total sputtering pressures were 2.2 and 9.2 mTorr for Cu_3N and SnN_x, respectively. A 76×26 mm^2 borosilicate glass plate was used as the substrate.

Thermal decompositions of the films were made in the chamber of the sputtering equipment. The chamber vacuum just before heating the films was less than 2.0×10^{-6} Torr to prevent oxidation of the metal at the time of formation. For the thermal decomposition, the 150-nm-thick Cu_3N films were heated at 470 °C for 10 min, and the 140-nm-thick SnN_x films were heated at 550 °C for 30 min. The softening of the glass substrate gave the latter temperature as the highest heating temperature in the experiments, although it is little lower than the temperature at the highest decomposition rate, 615 °C.[2] The laser writing was also performed in the chamber of the sputtering equipment by using an argon ion laser operating at power levels of 4 W on the 488 and 515 nm lines. The laser light was focused at 100 μm in diameter.

The crystallinity of the film was analyzed by the x-ray diffraction method with Cu $K\alpha$ radiation. The near-normal spectral reflectance of the film was obtained in the 0.19–3.2 μm range by means of an UV-VIZ-NIR recording spectrophotometer (Shimadzu UV 3100).

Figures 1(a) and 1(b) show the x-ray-diffraction patterns of the films on a borosilicate glass substrate. The Cu_3N film

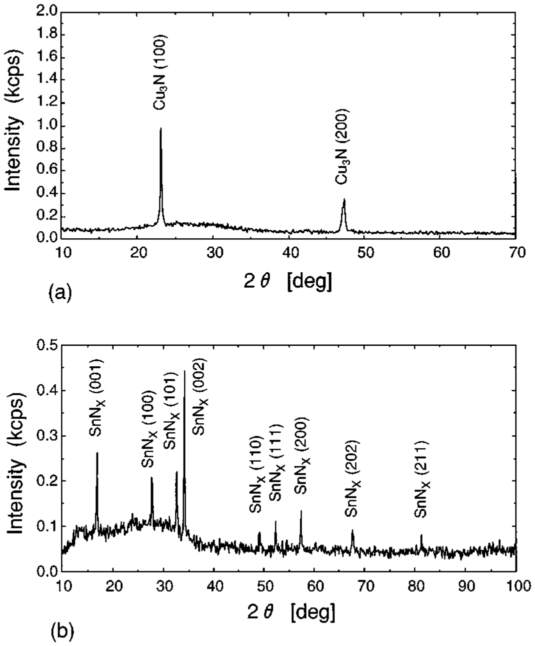

FIG. 1. X-ray-diffraction patterns of (a) Cu_3N and (b) SnN_x films on a borosilicate glass substrate.

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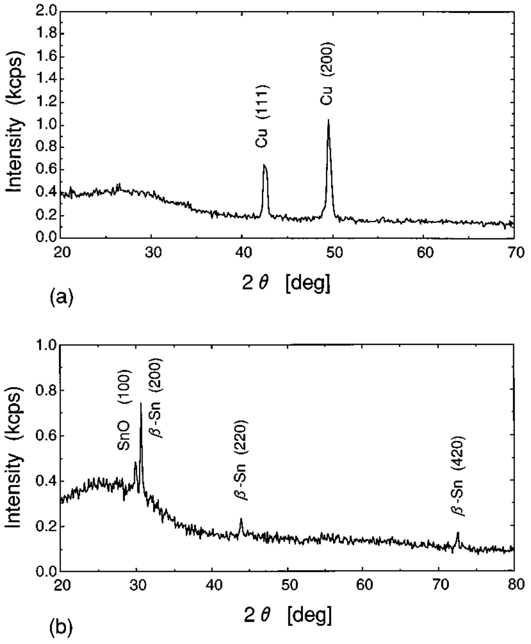

FIG. 2. X-ray-diffraction patterns of the films which were obtained by thermal decomposition of (a) Cu_3N film at 470 °C for 10 min and (b) SnN_x film at 550 °C for 30 min on a borosilicate glass substrate.

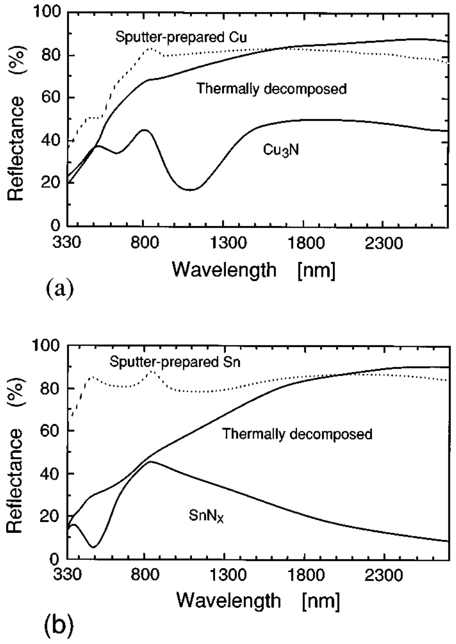

FIG. 3. Near-normal reflectance spectra of as-prepared (a) Cu_3N and (b) SnN_x films and of thermally decomposed films. Spectra of sputter-prepared (a) Cu and (b) Sn films are also shown.

is composed of crystallites with cubic structure[3] and with strong (100) plane texturing. The SnN_x film is composed of crystallites with hexagonal structure[4] and with strong (002) plane texturing. Details of the structures and properties of both Cu_3N and SnN_x films are described in the authors previous papers.[3,4]

The Cu_3N and SnN_x films were decomposed into Cu and Sn films by heating in vacuum. Besides, the metal spots were formed on both Cu_3N and SnN_x thin films by laser writings at energy density of 15–20 $\mathrm{kJ\,cm^{-2}}$. Figures 2(a) and 2(b) show the x-ray-diffraction patterns of the film after the thermal decomposition. There appear clear peaks for Cu and β-Sn without a trace of the peaks for Cu_3N and SnN_x. It is noted that a peak for SnO (100) is included in Fig. 2(b).

Figures 3(a) and 3(b) show the near-normal reflectance spectra of as-prepared Cu_3N and SnN_x films and of the thermally decomposed films. Also shown in Figs. 3(a) and 3(b) are the spectra of sputter-prepared Cu and Sn films. The reflectance spectrum of the Cu film obtained by thermal decomposition of Cu_3N film is close to that of sputter-prepared Cu film; and, the spectrum of the as-prepared Cu_3N film is smaller than those of Cu films. The difference in reflectance at about 800 nm between the as-prepared Cu_3N film and the Cu film is large enough to use as optical recording media. On the other hand, the reflectance spectrum of the Sn film obtained by thermal decomposition of the SnN_x film is very different from that of the sputter-prepared Sn film. The difference in reflectance at about 800 nm between the as-deposited and thermally decomposed film is not large enough to use as optical recording media. This is attributable to an inclusion of SnO in the Sn film. Oxygen is inferred to be included in the oxide layer at the surface of the SnN_x film before the thermal decomposition. In addition, some of the Sn formed in the thermal decomposition was observed to coalesce into a thick layer (or microscopic beads in laser writing) leaving areas where constrictions are evident. These phenomena are quite likely due to the relatively low melting point of Sn (232 °C) which is evidently exceeded during the thermal decomposition.[2] This phenomenon deteriorates the specular reflection at the surface.

In conclusion, the Cu_3N obtained by the reactive sputtering method can be decomposed into Cu by heating at 470 °C for 10 min, and the difference in reflectance between the as-deposited and thermally decomposed film is large enough to use as optical recording media. The Sn film obtained by thermal decomposition of SnN_x film, however, shows a small difference in reflectance from that of SnN_x film, because of an inclusion of SnO in the film. In addition, the melting of tin during the thermal decomposition deteriorates the specular reflection at the surface.

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