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Local structure of granular thin films containing transition metal nitride nanoparticle

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1 Introduction

Our group has reported a granular thin film including metallic TiN nanoparticles precipitated in insulating Si(N,O) amorphous matrix by thermal annealing of rf sputtered Ti-Si-(N,O) thin film. The granular thin films ranged from dark green, canary yellow, and to horizon blue in color depending on the annealing temperature. The color change in the annealed thin films is related to the surface plasmon resonance in the nanosized TiN particles dispersed in the insulating Si(N,O) matrix, similar to Au nanoparticle [1]. Transition metal nitrides, such as ZrN and NbN have been expected to be an alternatives for Au nanoparticle because of their metallic conductivity [2]. Precipitation behavior of the nitrides appeared to be different each other due to their different enthalpy of formation.

In this study, M-Si-(N,O) amorphous thin films (M= Zr, Nb) were prepared by rf sputtering deposition. They were post-annealed in evacuated silica tube to precipitate MN particles in an amorphous Si-(N,O) matrix. Their crystalline phase and optical property were studies in relation to their anneal temperature.

2 Experiment

Composite targets M/Si (M = Zr and Nb) were sputtered in N_2 at 2 Pa using rf-magnetron sputtering to deposit thin films on silica glass substrates under an applied rf power of 100 W. The as-deposited amorphous thin films were annealed in an evacuated silica tube at a pressure below 0.1 Pa in the temperature range from 700 ~ 1000 °C for 5 ~ 10 hours.

Crystalline phase was characterized by using X-ray diffraction. Transmittance spectra were measured by a UV-vis spectrometer. X-ray absorption spectra of Zr K- and Nb K-edges were observed in fluorescence mode at the beam lines 9C and NW10A in Photon Factory, in KEK. The spectra were analyzed using a program REX2000 [3]. Microstructural observation of the surface and cross section of the annealed thin films were performed by using FE-SEM.

3 Results and Discussion

As-deposited Zr-Si-(N,O) thin film was XRD amorphous and any crystalline phase did not appear in the post annealed products. Their transmittance spectra did not change significantly and preserved its high transparency in visible light. XANES spectra of the Zr-K edge of the annealed thin films were similar to that of ZrO_2 standard. Because ZrO_2 is thermodynamically stable than ZrN, ZrO_2-like amorphous Zr-(N,O) particles precipitated in a Si(N,O) matrix by thermal annealing.

As-deposited and post annealed Nb-Si-(N,O) thin films were also amorphous in XRD. Their color was changed from yellow in the as-deposited thin film to brown in the annealed product at 700 °C. Thin film annealed above 800 °C showed golden color. Nb K-edge XANES spectra were observed to investigate the local structure around Nb and formation of NbN nano particles by the post annealing process. Nb_2O_5 standard has a characteristic shoulder peak at around 18974 eV which has been assigned to a transition of 1s $\rightarrow$ 4d [4]. The similar shoulder peak appeared in the as-deposited Nb-Si-(N,O) thin film as shown in Fig. 1(b). The intensity decreased with increasing the annealing temperature and disappeared above 800 °C. Characteristic peak labeled as A in the Fig. 1(a) for rock salt type δ-NbN [5] was clearly observed in the annealed products above 800 °C. Rock salt type NbN nanoparticles were precipitated from Nb-Si-(N,O) amorphous thin film to form a granular structure by the post annealing. The color change of the annealed tin films might be related to a surface plasmon resonance of NbN nanoparticles.

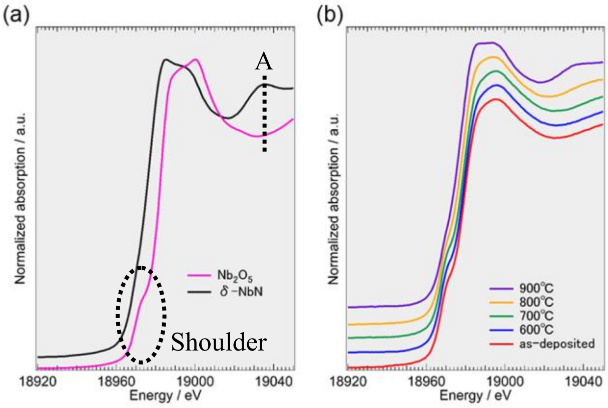

Fig. 1 XANES spectra of the Nb K-edge of the standards (a) and Nb-Si-(N,O) thin films (b).

References

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