Selective fabrication of Ca_2NH and CaNH epitaxial thin films using reactive magnetron sputtering

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[Introduction] Calcium compounds combined with nitrogen and hydrogen attract attention as promising catalysts for NH_3 conversion. Among them, Ca_2NH and CaNH exhibit high catalytic performance in NH_3 synthesis and decomposition, respectively [1,2,3]. To quantitatively understand the mechanism of the catalytic reactions, epitaxial thin film surfaces provide an ideal platform due to well-defined size and crystal orientation. To date, however, neither Ca_2NH nor CaNH thin films have been reported. In this study, we report the selective fabrication of Ca_2NH and CaNH epitaxial thin films using reactive magnetron sputtering.

[Experiment] Ca-N-H epitaxial thin films were deposited on MgO(110) substrates using reactive magnetron sputtering. A Ca metal plate (diameter of 1 inch) was used as a target material. The substrate temperature was set to 400 ºC, and RF power of 30 W was supplied. The total pressure was set to 1.0 Pa, and the partial pressures of Ar, N_2, and H_2 gases (P_{Ar}, P_{N2}, and P_{H2}, respectively) were varied to explore the growth conditions. The structural properties were characterized by X-ray diffraction (XRD) and Raman spectroscopy. Chemical compositions were evaluated using Rutherford backscattering spectroscopy (RBS), elastic recoil detection analysis (ERDA), and nuclear reaction analysis (NRA). Due to the air-instability of the thin films, air-tight cells were used for the characterizations.

[Results and discussion] Figure 1a shows out-of-plane XRD patterns of thin films fabricated at different P_{H2} (0.02 – 0.38 Pa). At lower H_2 partial pressure (P_{H2}) of 0.020 Pa, we observed a diffraction peak at $2\theta = 50.9°$. As P_{H2} increased to 0.074 Pa, the 2θ position was shifted to 49.9°, suggesting the phase transition from Ca_2NH ($2\theta_{440}$ = 51.0°) to CaNH ($2\theta_{220}$ = 50.1°). Raman spectroscopy supports this phase transition scenario: a sharp peak corresponding to Ca_2NH appears at 321 cm^{-1} [1] for P_{H2} = 0.020 Pa, whereas the peak is diminished as P_{H2} increased. The chemical compositions of thin films fabricated under P_{H2} = 0.020 and 0.074 Pa were $CaN_{0.55}H_{0.37}$ (~$Ca_2N_{1.1}H_{0.73}$) and $CaN_{0.85}H_{0.82}$, respectively. These results indicate that P_{H2} plays an important role in selective control of the Ca_2NH/CaNH phases in thin films. To the best of our knowledge, this study is the first report of metal-nitrogen-hydrogen epitaxial thin films.

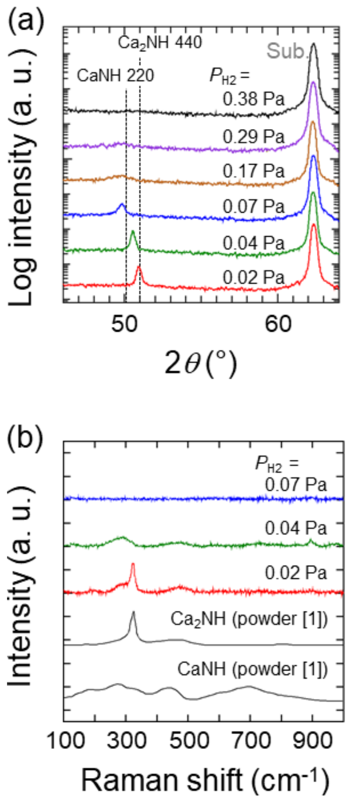

Fig. 1 P_{H2} dependence of (a) Out-of-plane XRD patterns and (b) Raman spectra.

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