Selective fabrication of Ca_2NH epitaxial thin films using magnetron sputtering system

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Ca_2NH is a promising catalyst for the production of NH_3, which is an important chemical such as fertilizers and hydrogen storage [1]. To quantitatively understand the mechanism of the catalytic reactions, epitaxial thin film surfaces can provide an ideal platform due to well-defined size and crystal orientation. However, Ca_2NH thin film has not been reported to date. In addition, due to the structural similarity between Ca_2NH and CaNH, it is difficult to selectively stabilize the Ca_2NH phase using epitaxial effects. In this study, under various gas conditions, we study a route to selectively fabricate Ca_2NH epitaxial thin films using reactive magnetron sputtering.

Ca-N-H 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_{N_2}, and P_{H_2}, respectively) were varied to explore the growth conditions for Ca_2NH phase. The structural properties were characterized by X-ray diffraction (XRD) and Raman spectroscopy. Due to the air-instability of the thin films, air-tight cells were used for the characterizations.

Figure 1a shows out-of-plane XRD patterns of thin films fabricated at different P_{H_2}/P_{N_2} (0.033 - 1.00). A peak appeared at $2\theta \sim 50.9°$ for $P_{H_2}/P_{N_2} = 0.033$, suggesting Ca_2NH 440. As P_{H_2}/P_{N_2} increased to 0.13, the peak position was shifted to a lower angle (~ 49.9°), suggesting the phase transition from Ca_2NH to CaNH. Note that there is almost no peak in higher P_{H_2}/P_{N_2}.

This phase transition scenario is also confirmed by Raman spectroscopy. In Figure 1b, a sharp peak appears at 321 cm^{-1} for $P_{H_2}/P_{N_2} = 0.033$, corresponding to Ca_2NH [1], whereas the peak is diminished as P_{H_2}/P_{N_2} increased. Namely, Ca_2NH thin film is selectively fabricated in $P_{H_2}/P_{N_2} = 0.033$. To the best of our knowledge, this study is the first report of metal-nitrogen-hydrogen epitaxial thin films.

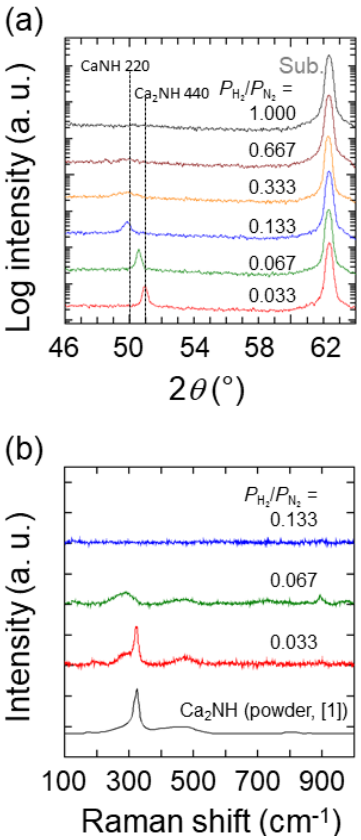

Fig. 1 P_{H_2}/P_{N_2} dependence of (a) Out-of-plane XRD patterns and (b) Raman spectra

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