LPMOCVD에 의한 Nb_2O_5 박막성장의 반응공학적 모델링

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Reaction engineering modeling of LPMOCVD of Nb_2O_5 thin film

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INTRODUCTION

Niobium oxide(V) is one of the components of the stoichiometric complex oxide lithium niobate($LiNbO_3$). Because a thin film of $LiNbO_3$ is of potential use both as a waveguide and as a modulator, several attempts at growing thin films of $LiNbO_3$ have been studied. The growth methods reported so far include the epitaxial growth from a melt, sputtering, a vapor transport technique, sol-gel method and a recently, low pressure metal-organic chemical vapor deposition(LPMOCVD) has been reported[1]. However, these authors gave no information on the reaction engineering model of the LPMOCVD. In order to design a CVD reactor and to determine optimum operating conditions, it is necessary to develop a model which quantitatively describes the reaction and transport phenomena in any type of CVD reactor.

In this work, a preliminary experiment was conducted on the deposition behavior of Nb_2O_5 film using bis-dipivaloylmethanate niobium trichloride($Nb(C_{11}H_{19}O_2)_2Cl_3$: $Nb(DPM)_2Cl_3$ hereafter) as a source material, and the gas phase and surface reactions were analyzed by a micro/macro simulation method which has been developed by the authors.[2,3]

EXPERIMENTAL

The schematic of the LPMOCVD apparatus used in the present study is shown in Figure 1. The local growth rate distributions along the flow direction were measured by the weight change of each short tube before and after the experiment. In some cases, silicon substrates and silicon substrates with trenches were used. the films grown on Si substrates were used for characterization and surface reaction analysis. The vaporized source material was carried over to the reactor by nitrogen gas and was diluted

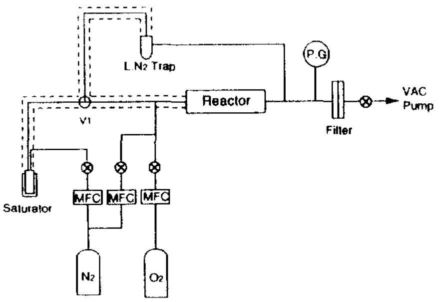


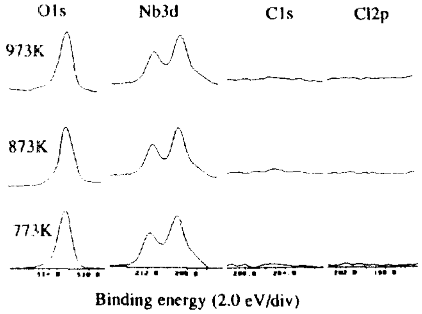
Figure 1. Schematic of LPCVD experimental apparatus.

further with nitrogen and oxygen just before the reactor tube inlet.

The crystal structure was characterized by X-ray diffraction(XRD). The step coverage of the film on the trenches was observed using a scanning electron microscope(SEM), and the morphology of the grown films was observed by the tapping mode atomic force microscope(TAFM). The composition of the film was analyzed by the X-ray photoelectron spectroscopy(XPS).

EXPERIMENTAL RESULTS

Narrow range XPS spectra of the Nb_2O_5 films deposited at various temperatures are shown in Figure 2. A small peak of Cl(2p) along with C(1s) appears in the spectrum indicating that very small amounts of carbon and chlorine are included in the bulk film. However, the XPS spectrum taken at the asgrown surface shows distinguishable peaks of carbon and chlorine. Figure 3 shows the XRD patterns. All peaks are assigned to Nb_2O_5. Figure 4 shows TAFM images of the Nb_2O_5 films grown at different temperatures. The crystallinity and the morphology of the niobium oxide film changes with increasing temperature from the nodule-shaped crystals grown at 773K to more well-defined crystals. The growth rate distributions along the flow direction are shown in Figure 5, in which each histogram, whose width equals to the length of the short quartz tubes, represents the



※Etching source : ion-gun [Ar^+], 2.0kv 30.0mA
Etching time : 5min

Figure 2. The narrow-range XPS spectrum of the Nb_2O_5 films grown at various temperatures.

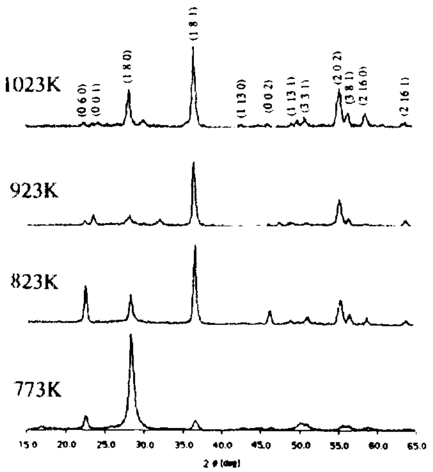
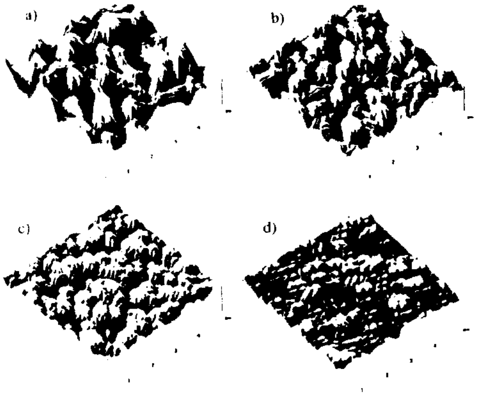


Figure 3. XRD pattern of the Nb_2O_5 films grown at various temperatures.



X : 1.0 μm/div, Z : 500 nm/div

Figure 4. AFM images of the Nb_2O_5 films grown at different temperatures.

local growth rate.

CVD REACTION MODEL

We assume that the CVD can be modeled by a simple reaction model. The source material A,($Nb(DPM)_2Cl_3$) undergoes a gas phase reaction to an active intermediate,B.

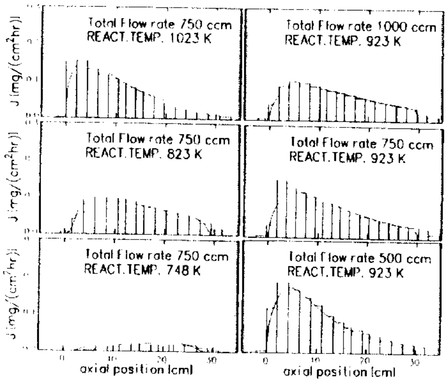


Figure 5. Growth rate distribution of Nb_2O_5 film along the flow direction.

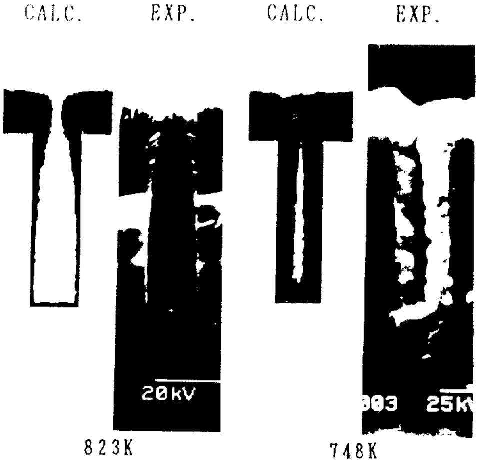


Figure 6. Observed and simulated step coverages on micro-trenches grown at 5 torr under different temperatures.

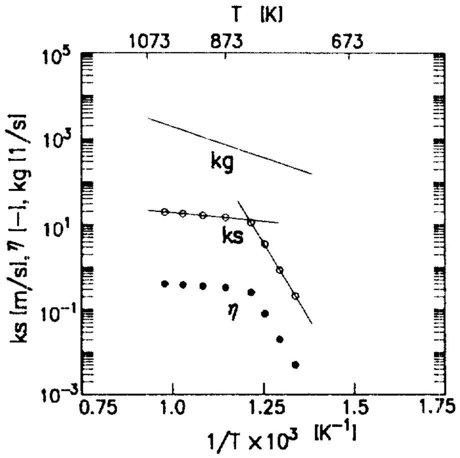


Figure 7. Arrhenius plots for reactive sticking cdefficient,surface reaction constant and gas-phase reaction constant.

B is transported by convective diffusion to the tube wall and changes to a solid product(Nb_2O_5) through a surface reaction. We used a Monte Carlo step coverage simulation to analyze the surface reaction by means of the profile fitting of the film grown on micro trenches. The experimentally observed profiles of the Nb_2O_5 film grown at different temperatures together with the calculated profiles are shown in Figure 6. The film profile and the value of η shown in the figure represent the best results optimized through the repeated profile fitting simulations. The reactive sticking coefficients and surface reaction rate constants of this CVD system thus determined are plotted in Figure 7. The lines in the figure correspond to the followings;

$$T > 826K \quad ks = 114 \exp(-15\ 000/RT) \tag{1}$$

$$T \leq 826K \quad ks = 1.5 \times 10^{18} \exp(-270\ 000/RT) \tag{2}$$

The gas phase reaction rate constant kg was chosen as the single adjustable parameter in a macro-scale simulation code[4], in which heat and mass transfer, gas phase and surface reactions are all taken into account. The solid curves shown in Figure 5 represent the optimized results of the macro-scale simulation. The numerical simulation reproduces all experimental results by choosing the gas phase reaction rate constant as

$$kg = 1.4 \times 10^6 \exp(-56\,000/RT) \qquad (3)$$

Figure 7 includes the Arrhenius plot of the gas phase reaction rate constant, eq.(3).

CONCLUSIONS

We have studied the growth mechanism of niobium oxide thin films grown by a thermal LPMOCVD using the β-diketonate complex. The yield of Nb_2O_5 film is almost independent of the oxygen concentration in the gas phase. XPS indicates that there are trace inclusions of carbon and chlorine in the bulk film. The molecular mass and size of the intermediate are very close to those of the $Nb(DPM)_2Cl_3$ monomer. The micro-trench methodes revealed that the surface reaction rate constants is expressed by eqs.(1) and(2). By means of the macro scale simulation the gas phase reaction rate constant was determined as eq.(3)

REFERENCES

1) Takagi, T., Kobayashi, I., Tominaga, K. and Okada, M.: *Chem. Soc. Jpn.*, 7, 831(1993).
2) Jung, S. C., Imaishi, N. and Park, H. C.: *Kagaku Kogaku Ronbunshu*, **21**(1), (1995) in press.
3) Jung, S. C., Imaishi, N. and Park, H. C.: *Kagaku Kogaku Ronbunshu*, **21**(2), (1995) in press.
4) Akiyama, Y., Nakano, K., Sato, T. and Imaishi, N.: *Kagaku Kogaku Ronbunshu*, **18**, 840(1992).