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Theoretical Analysis and Experimental Monitoring of Morphology Change of Thin Film during Deposition
成膜時の薄膜形態変化の理論的解析と実験によるモニタリング

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1. Introduction

Metallic thin films often show the Volmer-Weber growth during deposition.[1] In the growth mode, deposited atoms first form clusters on the substrate surface (island structure). Then, the clusters become larger, and coalescence of the clusters occurs, forming a continuous film. Recently, properties of nanostructures that are obtained by stopping deposition around the transition between the island structure and a continuous film are studied, because it shows unusual behaviors and it can be applicable to several devices, such as the gas sensor[2]. For developing the devices, a measurement method that observes the morphology change during deposition is required to obtain nanostructures possessing desired properties.

We previously developed the *in situ* method that observes the transition of deposited material on piezoelectric materials.[3] In the study, we monitored changes in resonant frequency and internal friction of a piezoelectric substrate during deposition, and observed that resonant frequency decreases and internal friction shows a maximum, when the transition from the island structure to a continuous film occurs. Using the method, we observed that thickness at which a continuous film is formed differed depending on deposition materials. In this study, cause of the different film-growth behavior is theoretically and experimentally evaluated. We expect that differences in the size and the number of clusters formed during deposition are causes of the different behavior. If relationship between the structure of the deposited material and resonant frequency and internal friction of the substrate is clarified, detailed structure can be identified during deposition by using the developed method.

We establish a model that reproduces the growth of clusters using numerical analysis, and evaluate how material properties and deposition condition affect the formation of a continuous film. We also conduct experiments at different conditions, and compare the results to the calculation results to confirm the validity of the established model.

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2. Theoretical Analysis

We established a film-growth model that is based on Becker-Döring theory [4,5]. In the model, single atoms are deposited on a substrate, and they diffuse on it. When two atoms impinge, nucleation occurs. Then, clusters grow by capturing single atoms diffusing on the substrate; for example, a cluster consisting of N atoms at time t becomes a cluster consisting of $N + 1$ atoms at time $t + \Delta t$ by capturing a single atom. The growth rate depends on the cluster size; a larger cluster captures a single atom with higher probability. Because the growth rate depends on areal density of single atoms, the deposition rate F is a parameter. Surface diffusion coefficient D is also an important parameter; as D increases clusters grow faster. D depends on the activation energy E_d of deposited material and temperature T of the substrate as follows,[1]

$$D = D_0 \exp(- E_d / k_B T) \qquad (1)$$

where D_0 is diffusion constant and k_B is the Boltzmann constant.

We assumed that clusters grow three-dimensionally, and omitted the dissociation of an atom from islands. Then, assuming that the cluster shape is spherical crown, coverage on the substrate surface by clusters is calculated, and we decide that a continuous film is formed when the coverage becomes 80 %.

3. Experiments

For film-growth monitoring, we used the resonant vibration of piezoelectric material. **Figure 1** shows the schematic of the developed sensor. We used the lithium niobate as piezoelectric material. The size was 2.5 mm × 1.7 mm × 0.2 mm. We place the lithium niobate on the antennas. By applying an alternating electric field to the lithium niobate from an antenna, it oscillates due to the inverse piezoelectric effect. After stopping application of the field, it vibrates with attenuating. Then, an electric field is generated around the lithium niobate, and it

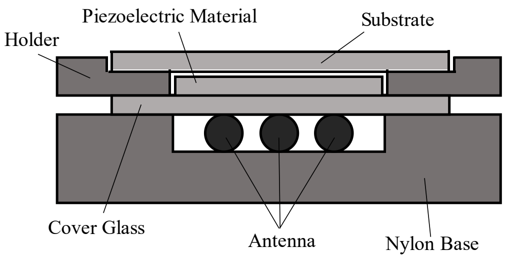

Fig. 1 Schematic of the sensor.

is detected by the other antenna. Resonant frequency and full width half maximum (FWHM) are determined from a resonant spectrum measured by sweeping the frequency of the applied field. In this experiment, we deposited Ag on silica glass at room temperature and -30 °C by magnetron sputtering. Sputtering power was 20 W, and Ar pressure was 0.4 Pa.

4. Results and Discussion

Figure 2 shows the FWHM measured during deposition at room temperature and -30 °C. In both results, a maximum appears clearly. According to the previous study[3], the peak indicates that a continuous film is formed. The time is 344 and 280 s, respectively, and a continuous film is formed at smaller thickness at lower temperature.

In the theoretical analysis, we calculated the change in the number of clusters with time at various surface diffusion coefficients. The number of the clusters composed of N atoms per unit area $n_N(t)$ at 20 seconds is shown in **Fig. 3**. It is clearly observed that as D becomes larger, clusters tend to be larger.

Then, the time at which a continuous film is formed was deduced, and it was 44.9, 31.6, and 22.4 s at D = 1.0, 0.1, and 0.01 μm²/s, respectively. This result indicates that when cluster-growth speed is

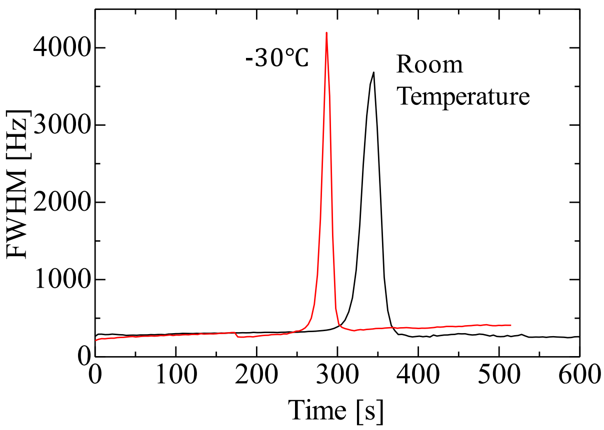

Fig. 2 Change of FWHM during deposition at room temperature and -30 °C.

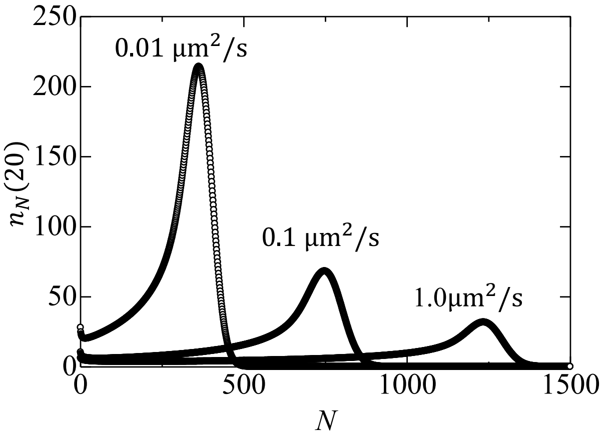

Fig. 3 Distributions of the number of clusters at 20 s with different surface diffusion coefficients.

higher, a continuous film is formed slower. Considering that when a larger cluster is formed, cluster height becomes larger in addition to the contact area with the substrate, making coverage relatively small, the calculation result is qualitatively explained.

According to Eq. (1), D decreases with decreasing T; lower substrate temperature decreases D. In the experiment, a continuous film was formed earlier at lowered temperature. This trend is the same as the calculation result, and it confirms the validity of the developed model.

5. Conclusion

In this work, the results of the theoretical analysis showed the same trend as the experimental results, and we could reproduce the formation of a continuous film. Then it was shown that the diffusion coefficient influences the growth of clusters and the formation of the continuous film. In this calculation, we didn't consider dissociation of an atom from an island, coalescence of islands and so on. So if we establish a model that includes these factors, the model may reproduce the experimental results more precisely.

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