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Formation process of alloy nanoparticles synthesized by sputtering: noncontact monitoring using resonant ultrasound spectroscopy

スパッタリングによる合金ナノ粒子の形成プロセス：超音波共鳴法による非接触観察

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1. Introduction

PdAu alloy nanoparticles show unique properties, and several studies have been performed on PdAu alloy nanoparticles. For example, it is reported that the cross-coupling reaction using PdAu alloy nanoparticles is more efficient than that using Pd nanoparticles[1], and PdAu nanoparticles are used as a catalyst to reduce sulfite in water[2]. It is expected that PdAu nanoparticles enhance the surface-enhanced Raman scattering effect[3]. Application of PdAu nanoparticles to hydrogen sensors is also studied[4].

Alloy nanoparticles can be synthesized by several methods. Sputtering of two metals simultaneously on a substrate is one of the methods. Using the sputtering, the composition can be changed by changing target metals, and the composition ratio can be changed by controlling the sputtering rates. These features are suitable for fabricating alloy nanoparticles of desired composition. However, formation process of alloy nanoparticles by sputtering has not been understood completely.

When the metals are sputtered on a substrate, atoms diffuse on the substrate and alloy nanoparticles are formed through nucleation and nucleus growth. Internal structure of alloy nanoparticles then becomes disordered structure (**Fig. 1** (a)), core-shell structure (**Fig. 1** (b)), and so on, depending on the composition and sputtering conditions. Because the properties of alloy nanoparticles change depending on the internal structure, it is important to understand the formation process of alloy nanoparticles to obtain desired internal structures and properties. However, it is not straightforward to observe the formation process of alloy nanoparticles during sputtering. For this reason, the formation process has not been clarified. Under the circumstances, in this study, we observed the formation process of PdAu alloy nanoparticles in real time during sputtering using the resistive spectroscopy method[5], and internal structure of PdAu alloy nanoparticles is investigated.

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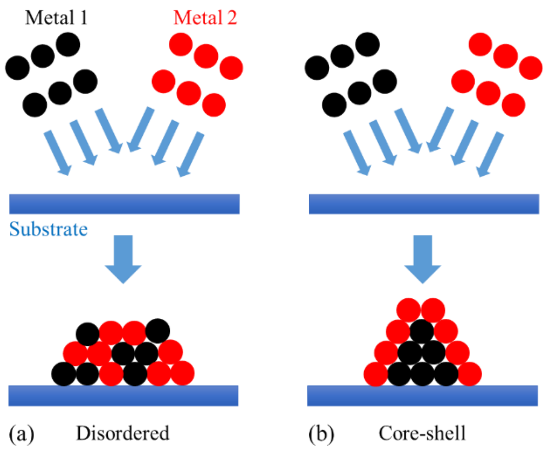

Fig. 1 Schematics of internal structure of bimetallic alloy nanoparticles. (a) Disordered structure and (b) core-shell structure.

2. Experimental principle

We propose observation of nanoparticle shape for investigating the formation process. When nanoparticles are formed on a substrate, their shape should change depending on the surface energy of the nanoparticles. Because the surface energy differs for each metal, the surface energy of nanoparticles should change depending on the composition on the surface. Therefore, shape of nanoparticles should change depending on the composition on the surface (Fig. 1). According to this idea, by evaluating the composition on the surface by measuring the nanoparticle shape, we will be able to estimate the internal structure of the nanoparticles.

However, it is quite difficult to directly observe the nanoparticle shape during sputtering. To solve this problem, we used the resistive spectroscopy method[5]. In this method, nanoparticle shape is evaluated by measuring the resonant properties of a piezoelectric material placed below a substrate. When an AC electric field is applied to the piezoelectric material, the piezoelectric material oscillates at the same frequency as the electric field due to the piezoelectric effect. Then, an oscillating electric field is excited around the piezoelectric material. The field reaches at the substrate surface, and electrons are moved between nanoparticles (tunneling current). Then, attenuation of the resonant vibrations is increased. Electrical resistance between nanoparticles changes depending on gap distances between nanoparticles, and degree of the attenuation changes depending on the electrical resistance. Therefore, gap distances between nanoparticles can be evaluated by measuring the attenuation of a resonant vibration.

Figure 2 shows typical resonant spectra obtained during sputtering of Pd and Au simultaneously on Al_2O_3 substrate. $LiNbO_3$ was used as a piezoelectric material, and resonant spectra were measured using line antennas. When the height of PdAu nanoparticles became 2 nm, the resonant peak become broader transiently. Evolution of full width at half maximum (FWHM) of the corresponding resonant spectrum is shown in **Fig. 3**. A peak appeared around 196 s, being corresponding to 2 nm thickness. In our previous work[5], we confirmed that the FWHM peak appears when nanoparticles contact one another. We consider that the timing of the FWHM peak changes depending on the nanoparticles shape. For example, when nanoparticle is elongated on the substrate (pan-cake shape), gaps between nanoparticles close on a short time, and an FWHM peak appears at smaller height. For this reason, by measuring the timing of the FWHM peak, we will be able to evaluate the shape of nanoparticles, which results in the evaluation of the internal structure.

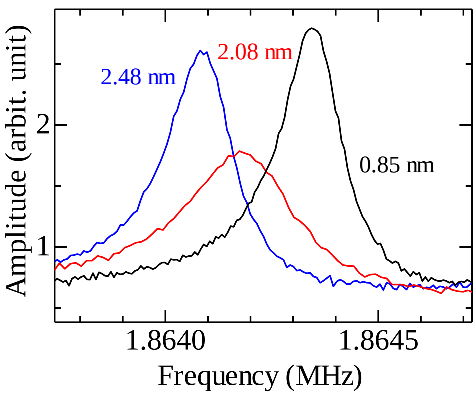

Fig. 2 Resonant spectra obtained during sputtering Pd and Au simultaneously.

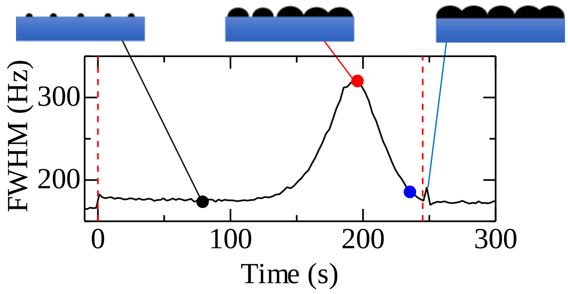

Fig. 3 FWHM during synthesizing PdAu nanoparticles. Pd and Au were sputtered during the time between dashed lines. Black, red, and blue plots correspond to the timing at which resonant spectra in Fig. 2 were obtained.

3. Synthesis of PdAu nanoparticles

PdAu nanoparticles were synthesized by RF magnetron sputtering. Two cathodes were attached to the sputtering chamber. First, we synthesized Pd and Au nanoparticles individually on an Al_2O_3 substrate. In the experiments, a FWHM peak appeared when the thickness was about 4 nm for Au nanoparticles and at 2 nm for Pd nanoparticles. Then, Pd and Au were sputtered simultaneously, and PdAu were synthesized. In the experiments, the timing of the FWHM peak did not change proportionally to the composition ratio, and the timing was close to that of Pd nanoparticles, which indicates that shape of PdAu nanoparticles is similar to that of Pd nanoparticles.

4. Summary

In this study, we observed that the timing of the FWHM peak changes depending on the composition. For analyzing the internal structure more detail, we would like to perform further experiments and simulation of the formation process using the molecular dynamics simulation.

References

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