In-Situ XPS Measurement of Co Nanoparticles Fabricated by Gas Evaporation Method*  
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The cobalt and cobalt nitride nanoparticles (NPs) have been fabricated by gas evaporation method under helium or nitrogen gases environment. These chemical states and compositions have been investigated by in-situ XPS and those distributions have been estimated by AFM. It is found that both cobalt and cobalt nitride NPs are slightly oxidized by the residual gas in the chamber. The cobalt nitride NPs fabricated under nitrogen gas are including the nitrogen atoms at 4.7% and the nitrogen atoms have the chemical bonding with the cobalt atoms.  
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I. INTRODUCTION  
The NPs have been paid attention as the attractive catalysts in many fields due to the large specific surface area bringing in high catalytic activities [1, 2]. Basically the fabrication methods of the NPs are liquid phase and gas evaporation methods [3, 4]. Since the liquid phase method is possible to mass-produce at a relatively low price, the method has been mainly used in the industrial fields. The NPs fabricated by the liquid phase methods have been covered with the surfactant to prevent from the aggregation each other. There is a possibility that the investigation of the catalytic reactions on the NPs is influenced by the interaction between the NP surface and the surfactant. In order to clarify the mechanism of catalytic reactions, it is important to investigate the surface chemical state of NPs with clean surfaces. The gas evaporation method is a suitable way to fabricate the NPs free from the surfactant.  

In this paper, we will apply the gas evaporation method for the fabrication of the cobalt NPs under helium atmosphere. From the standpoint of application, the cobalt NPs are well-known as a catalyst for many reactions, including Fischer-Tropsch process [5] and growth of carbon nanotubes [6]. And we will also try to fabricate the cobalt nitride NPs under nitrogen atmosphere. In order to investigate the chemical state and composition of the NPs, we will carry out the X-ray photoelectron spectroscopy (XPS) measurement without exposure to the air atmosphere as in-situ condition. The distributions of the NPs are estimated by atomic force microscopy (AFM) measurements.  

II. EXPERIMENTAL  
We have fabricated the cobalt and cobalt nitride NPs with clean surface by the gas evaporation method. Figure 1 shows a schematic view about the NPs fabrication system. The evaporation chamber was directly connected on the quick insertion chamber which had a role as the deposition chamber of the fabricated NPs, and these chambers

![FIG. 1: A schematic view about the NPs fabrication system.](image-url)
consisted of the NPs fabrication systems. To minimize the effect of residual gas, we performed pre-evacuation of the chambers down to about $10^{-5}$ Pa by the turbo-molecular pump. When we fabricated the NPs, the evaporation chamber was filled with the cooling gas such as He or N$_2$. In the evaporation chamber, the evaporated metals aggregated with each other by collision with the cooling gas and loss of their kinetic energies, and the metal NPs were synthesized. These NPs were transported through a narrow stainless steel pipe (the outer diameter was 1/8 inches) via the deposition chamber under vacuum environment of about 1 Pa and deposited on a substrate. Since the deposition chamber was connected on the XPS analysis chamber, the XPS measurements carried out without exposure under air atmosphere. The base pressure of the analysis chamber was about $2.0 \times 10^{-8}$ Pa. We fabricated Co NPs by heating twisted Co wires itself by resistance heating. The diameters of the Co wires were 0.50 and 0.25 mmϕ with 99.99+% purity. We describe the NPs fabricated by He gas under 50 Torr as CoNPs[He] and by N$_2$ gas under 25 Torr as CoNPs[N$_2$].

All samples were deposited on the Ni polycrystalline substrate for the XPS measurement and Si single crystal substrate for the AFM measurement. The NPs on Ni and Si were fabricated under the same conditions, which assured that the NPs on both substrates possessed same distributions of diameter and dispersion. The Ni polycrystalline substrates were cleaned by Ar$^+$ sputtering with 3 keV to remove impurities of sulfur, carbon and oxygen under an ultra-high vacuum condition, and subsequently carried out the fabrication of NPs and deposition on the substrate.

The Co wires and substrates were purchased from THE NILACO CORPORATION. The XPS measurements were carried out with the MgKα X-ray (1253.6 eV) and the hemispherical electron analyzer (PHOIBOS150, SPECS). The particle sizes were evaluated by AFM measurement for the height value of the NPs. The AFM measurement was carried out by NanoScope III-a (Veeco Instruments) with tapping mode.

### III. RESULTS AND DISCUSSION

The AFM images of the NPs were shown in Figs. 2(a) and (c). The light color points in the images show the NPs. We have estimated the size of the NPs by the value of the vertical direction because the value of the horizontal direction has larger error than that of vertical one. The histograms of particle height are shown in Figs. 2(b) and (d). We have eliminated the secondary particles which have been synthesized on the substrate surface under the deposition process. The estimated average diameters and standard deviations of them were 1.5 $\pm$ 0.3 and 2.4 $\pm$ 1.1 nm, respectively. These results show that the cobalt NPs which have small diameters with narrow distributions and high dispersion were fabricated under He or N$_2$ atmosphere. When the pressure of cooling gas in the fabrication chamber is reduced, the collision probability is dropped and the average diameter of NPs is

![AFM images and histogram of particle height](image-url)
The O 1s XPS spectra for the CoNPs[He] (a) and CoNPs[N2] (b).

The N 1s XPS spectra for CoNPs[N2].

smaller. Nevertheless, the NPs fabricated under N2 at 25 Torr were large in comparison with the one under He at 50 Torr. This is because molecular weight of the N2 is heavier than that of He, and has more high cooling probability.

Figure 3 shows the Co 2p XPS spectra for the CoNPs[He], CoNPs[N2] and standard sample of Co bulk. The spectrum for the CoNPs[He] has a small structure at higher binding energy position than the peak position of Co bulk at 778 eV and 793 eV. This result means that the CoNPs[He] are slightly oxidized. Because the cobalt evaporation source was heated for enough times to remove the oxidized surface before the deposition, this slight oxidation of NPs was caused by the residual gas in the fabrication chamber. The CoNPs[N2] were fabricated under same condition of CoNPs[He] except for the difference of cooling gases, therefore the CoNPs[N2] were also slightly oxidized. Figure 4 shows the O1s XPS spectra for the CoNPs[He] and the CoNPs[N2]. Those spectra are normalized by the intensity of each Ni 2p region. Both spectra have two peaks at 529.8 eV and 531.5 eV. The literatures reported that the former was corresponded approximately to Ni2O3 and the latter was corresponded approximately to NiO, CoO, Co2O3 and Co3O4 [7–10]. These spectra mean that the Ni substrates are oxidized. The O1s area of CoNPs[N2] is smaller than that of CoNPs[He]. This result means that the total oxidation of both the CoNPs[N2] and the substrate surface is smaller than that of the CoNPs[He]. Nevertheless the samples have similar degree of oxidation from the residual gases based on the same pre-evacuation manner, the oxidation degree is different. We speculate that the total oxidation of CoNPs[N2] are inhibited by the nitrogen gas. Both these O1s spectra and Co 2p spectra show the possibility of oxidation. The shape of the spectrum for the CoNPs[N2] resembles in that of the CoNPs[He]. To emphasize the effect of the nitride, we subtract the spectrum for CoNPs[He] from CoNPs[N2] and the subtracted spectrum is shown in Fig. 3(d). Figure 3(d) shows that the CoNPs[N2] have the structures at higher binding energy position than the peak position of CoNPs[He]. Other studies indicated that the Co 2p XPS spectra for the cobalt nitride had peaks around same as our structures [11, 12]. Figure 5 shows the N1s XPS spectrum for CoNPs[N2]. The spectrum is deconvolved into components of Gaussian peaks at 398.2 eV and 397.6 eV. These energy positions are corresponded approximately to another studies of cobalt nitrides [13, 14], and located at lower side than the nitrogen molecules (399 eV) [15]. The Co 2p XPS spectra for CoNPs[N2] are shifted to higher binding energy of bulk Co, and the N1s XPS spectra are shifted to lower binding energy of nitrogen molecules. This means that the cobalt atoms and nitrogen atoms included in NPs have chemically bonded each other. Judging from the value ratio of the N 1s and Co 2p peak areas and the atomic sensitivity factors of Co 2p and N 1s which are 3.590 and 0.477 [16], we estimate that the concentration of nitrogen atoms included in the CoNPs[N2] is 4.7%.

IV. CONCLUSION

We fabricate the CoNPs[He] and CoNPs[N2] by gas evaporation method under He or N2 atmosphere. The estimated average diameters and standard deviations of them are 1.5 ± 0.3 and 2.4 ± 1.1 nm, respectively. The cobalt NPs with small diameters, narrow distributions and high dispersion have been fabricated under He atmosphere. The CoNPs[He] and CoNPs[N2] are slightly oxidized by the residual gas in fabrication chamber. The CoNPs[N2] include the nitrogen atoms at 4.7%, and the nitrogen atoms have the chemical bonding with the cobalt atoms.
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