We demonstrate here a simple method to tune the optical properties of thin films of nickel nanowires grown inside an anodic alumina oxide (AAO) template using different anodizing conditions. The optical properties of the metal plate can be effectively tuned by adjusting the thickness of porous alumina oxide. In our case, the thickness of the porous alumina oxide depends strongly on the current density because the duration of anodization maintained constant. The transmission electron microscopic image of the cross section reveals the growth of nickel nanowires which are embedded in porous alumina oxide. Due to the interference between incident light and reflected light, the anodic alumina oxide plate exhibits a variety of color. This demonstration of optical behavior tuning makes it possible to scale up the preparation of metal/oxide nanostructures exhibiting color tuning in the visible region.

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**Experimental**

**Materials.**—Nickel sulfate heptahydrate (95%), ammonium sulfate (99.5%), boric acid (99.5%), and magnesium sulfate heptahydrate (99.5%) were obtained from Acros Organics and used without further purification. The water used throughout this work was reagent-grade deionized (DI) water produced by a Milli-Q SP ultrapure-water purification system of Nihon Millipore Ltd., Tokyo.

**Preparation.**—The AAO templates used for the electrodeposition of Ni nanowire arrays were prepared using aluminum 99% foils. Prior to anodization, the foils were degreased with acetone followed by washing with DI water for 15 min in the open air. The ordered porous alumina templates were prepared using the anodization process. Briefly, the clean aluminum foil was anodized in 10% H$_2$SO$_4$ aqueous solution under a constant current for 5 min at 18°C. Deposition was carried out at 20°C with an ac voltage of 14 V (50 Hz) and using Pb plate as a counter electrode and AAO template with aluminum plate as a working electrode. The deposition time was kept at 30 s. The electrolyte used to deposit Ni nanowires had the following composition: 25 g/L NiSO$_4$, 20 g/L MgSO$_4$, 25 g/L H$_3$BO$_3$, and 15 g/L (NH$_4$)$_2$SO$_4$. After electrodeposition, the AAO embedded nickel nanowires were washed with DI water and blown with nitrogen.

**Characterization.**—The morphology of AAO templates were characterized by field-emission scanning electron microscopy (FE-SEM, JEOL JSM-6700F). The Ni nanowires embedded in AAO templates were observed by transmission electron microscopy (TEM, PHILIP TECNAI F20) with an energy-dispersive X-ray analyzer (EDAX). All reflection spectra were recorded at room temperature on a Hitachi U-4100 spectrometer under 15° and 55° incidence angle at reflection mode.

**Results and Discussion.**

Figure 1 shows the typical top view of the SEM image of AAO templates prepared under 20 A/m$^2$ after moderate chemical etching in phosphoric acid solution. The ordered pore arrays as seen in Fig. 1 have identical pore diameters of about 8 nm, and the pore density...
The thickness of the oxide layer was found to be dependent on the current density of the experimental system if the current efficiency was ignored. The evolution of alumina oxide could be controlled by varying the current density of the anodizing experiment. A high-resolution TEM image and selected-area electron diffraction (SAED) of nickel nanowires were shown in Fig. 3. Selected-area electron diffraction was performed to reveal the crystalline nature of nickel nanowires embedded in AAO. The highly crystalline nature of the nanowires apparently corresponds closely to the pore diameter. These nickel nanowires were characteristic of the smooth surface of AAO, which clearly indicates the growth of nickel nanowires inside the channels of the alumina membranes. Figures 2a and c show TEM images of the cross section of nickel nanowires embedded in the AAO template prepared under different current densities of 20 and 100 A/m², respectively. Figures 2b and d show magnification images corresponding to Fig. 2a and c, respectively. As shown in Fig. 2a, the growth of nickel nanowires can be clearly observed from the bottom of the alumina template. A statistical analysis of hundreds of nanowires from Fig. 2b and d indicate uniform lengths of nickel nanowires in each sample (Fig. 2a, a mean length around 122.9 nm with a standard deviation of 2.7 nm, and Fig. 2c, a mean length around 124.5 nm with a standard deviation of 3.3 nm). Because we have used constant electrodeposition time and applied voltage for nickel deposition, the thicknesses of nickel embedded in the alumina template in each sample were found to be similar to each other. In fact, we have obtained an alumina template as thick as 1361.5 nm at current density of 100 A/m², as shown in Fig. 2d, noting that some darkness in the nickel nanowires reflected the intensity of scattered electrons from a different substance and is proportional to the crystalline properties of nickel nanowires. The TEM images of a cross section of nickel nanowires embedded in the AAO template prepared under a current density of 100 A/m² are shown in Fig. 2c and d. The thickness of alumina oxide could be further increased to 1361.5 nm (with a standard deviation of 2.3 nm) if a constant current density is increased to 100 A/m². In this case, the increase in thickness of alumina oxide was believed to be related to the growth of alumina oxide due to the oxidation of aluminum. The increase in oxide thickness, which played an important role in determining the optical feature of aluminum foil, might also be involved in the etching process of sulfuric acid at the interface of oxide/electrolyte during porous oxide growth. Due to the constant duration of porous oxide growth, the total electrons applied to oxidize the aluminum foil would be proportional to the current density of the alumina template. Thus, the thickness of the alumina template could be controlled by varying the current density of the anodizing experiment. A high-resolution TEM (HRTEM) image and selected-area electron diffraction (SAED) of nickel nanowires were shown in Fig. 3. Selected-area electron diffraction was performed to reveal the crystalline nature of nickel nanowires embedded in AAO. The highly crystalline nature of the nickel nanowires reflected the intensity of scattered electrons from a different substance and is proportional to the crystalline properties of nickel nanowires. The TEM images of a cross section of nickel nanowires embedded in the AAO template prepared under a current density of 100 A/m² are shown in Fig. 2c and d. The thickness of alumina oxide could be further increased to 1361.5 nm (with a standard deviation of 2.3 nm) if a constant current density is increased to 100 A/m². In this case, the increase in thickness of alumina oxide was believed to be related to the growth of alumina oxide due to the oxidation of aluminum. The increase in oxide thickness, which played an important role in determining the optical feature of aluminum foil, might also be involved in the etching process of sulfuric acid at the interface of oxide/electrolyte during porous oxide growth. Due to the constant duration of porous oxide growth, the total electrons applied to oxidize the aluminum foil would be proportional to the current density of the alumina template. Thus, the thickness of the alumina template could be controlled by varying the current density of the anodizing experiment. A high-resolution TEM (HRTEM) image and selected-area electron diffraction (SAED) of nickel nanowires were shown in Fig. 3. Selected-area electron diffraction was performed to reveal the crystalline nature of nickel nanowires embedded in AAO. The highly crystalline nature of the
as-deposited samples was investigated by the SAED measurements and many individual nanowires were characterized. The diffraction rings shown in Fig. 3 confirm that the nickel nanowires are polycrystalline and indicate that the structure of as-prepared nanowires is face-centered cubic, which is consistent with the HRTEM result. This result implied that nickel nanowires are polycrystalline, which is in accordance with result of TEM. The lattice plane distances derived from the diffraction rings of the as-deposited nanowires fit well to the formula \( d = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \), where \( h, k, \) and \( l \) are the indexes noted in the diffraction pattern and \( a \) is the lattice constant, which indicates that nickel nanowire has a face-centered cubic structure.

We could also conveniently monitor the nanostructures of the alumina template by UV-visible spectroscopy because the nanostructures of nickel nanowires embedded in the alumina template exhibit distinctive reflection peaks in the UV-visible region that are strongly dependent on their structure (e.g., thickness of reflection layers). The interference among reflecting light having different optical pathlengths leads to the appearance of distinct color (as shown in Fig. 4). The optical properties of the alumina template were not only dependent on the thickness of alumina but also on the deposition of metal. The ultrathin film greatly enhances the reflection spectra due to the metal deposition on the surface of the porous template during the electrochemical deposition of nickel. Moreover, the porous alumina template was antibacterial because of silver nanowires grown in the pores. This multifunctional approach was expected to be useful in many related fields as desired metal can be electrodeposited into the porous template, achieving different properties. Figures 5a and b show the reflection spectra recorded from the nickel nanowires embedded in the alumina template prepared under a current density of 20 and 100 A/m², respectively. The reflection spectra were collected from different angles of incident (15 and 55°) and the spectra would exhibit specific optical properties due to the different optical path. The insert shows the photograph of a metal plate from a different observable angle, which indicates that the color was strongly dependent on the observable angle. As shown in Fig. 5a, the color of the metal plate changed from purple to maroon as the observable angle changed from 15 to 55°. A similar observation was obtained in Fig. 5b, where the color was evolved from yellow to green. The comparison of the reflection spectra of the alumina template (Fig. 5a and b) prepared under different current densities confirmed that reflection spectra were strongly dependent on the nanostructures. According to Bragg’s law

\[
2d \sin \theta = n\lambda
\]

where \( d, n, \theta, \) and \( \lambda \) are lattice spacing (correspond to \( d \) in Fig. 3), an order of diffraction, diffraction angle, and wavelength. Each reflection peak represents a different order of diffraction. When \( d \) was a constant, different reflection wavelengths were detected at different observable angles. By using naked eyes to monitor the specific optical template, the color observed by naked eyes was a mixture of all reflection light. Because the reflection properties greatly depend on the thickness of oxide layers (corresponding to \( d \) value in Fig. 4), the color of the metal plates could be controlled by the synthesis conditions (e.g., current density, anodizing voltage, and anodizing time).

One of the important features is that these nanostructures could be used to tune the color over a broad range. Figure 6 shows the photograph of fourteen metal plates of such nanostructures, showing that the color could be tuned to change from blue to orange to yellow. The tuning of optical properties was mainly accomplished by the structural fabrication from oxidation of aluminum metal to grow pores, through electrodeposition of nickel nanowires inside porous AAO. This demonstration of optical tuning in the visible range was not only useful for producing desired colors but also for creating novel multifunctional materials that could be used for various applications.
region makes it easier to scale up the preparation of metal/oxide nanostructures, which may have potential commercial applications.

Conclusions

We have systematically investigated the structural and spectral changes involved in the anodizing (different current densities) and electrodeposition conditions. The nickel nanowires can grow from the bottom of the porous alumina template under ac. The different current densities would result in the difference in thicknesses of the bottom of the porous alumina template under ac. The different electrodeposition conditions. The nickel nanowires can grow from the bottom of the porous alumina template under ac. The different current densities would result in the difference in thicknesses of the bottom of the porous alumina template under ac. The different electrodeposition conditions. The nickel nanowires can grow from the bottom of the porous alumina template under ac. The different current densities would result in the difference in thicknesses of the bottom of the porous alumina template under ac.

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