Color change mechanism of metal films – silver and niobium

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Abstract

We have studied the color change of silver films using sulfide solutions. In this present work, using a goniophotometer, we confirm that the color change of the film comes from thin film interference between silver sulfide and silver layers. In addition, the same procedures were carried out with niobium oxide and niobium films as the standard for comparison which is known to exhibit various colors due to thin film interference.

1. Introduction

It is generally known that silver (Ag) films are easily sulfurized in the presence of sulfide and turn their silver surfaces to spotted black ones. This is generally undesirable because the changeable color is limited to black and the color leads Ag films to lose the gloss on their surfaces. By contrast we have discovered a novel method for preparing silver films which have various colors with keeping their glosses [1]. In this method, Ag films made by sliver mirror reaction are colored by dipping them in specific aqueous solutions of sulfides. The color of the films, initially silver changes to yellow, red, and blue.

It is of great scientific interest to elucidate the mechanism of the color change of the silver films. In order to address the mechanism, these silver films have been characterized in terms of their surface morphologies and chemical compositions by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS) [2]. While the surface morphologies observed by SEM and TEM show the possibility that the color change of Ag films comes from the surface plasmon resonance [3] due to the particle size change of surface Ag nanoparticles, the surface chemical compositions determined by XPS analyses suggest that the color change of the Ag films is mainly due to the thin film interference between Ag and Ag_2S layers. We reported, in our previous paper [4], the possibility that the color change of the Ag films come from not surface plasmon resonance due to the particle size change of the Ag nanoparticles but the thin film interference between Ag and Ag_2S layers.

On the other hand, it is well-known [5] that anodically-oxidized niobium (Nb) films make various colors because of thin film interference between Nb and Nb_2O_5 layers. Therefore, we think that we can refer the color change of Nb films in order to address the color change mechanism of Ag films. In this present work, we explore the possibility that the primary cause of the color change of Ag films is the thin film interference.

2. Experiment

2.1 Coloration and characterization of Nb films

Nb films prior to the color treatment were made on ca. 10 x 50 mm aluminum plates by Nb deposition as described in the literature [5]. Typical procedures for coloring Nb films by anode oxidization were carried out as follows: a Nb film on aluminum plate as the anode electrode was dipped in a 50 ml of a 5.0 w/w% ammonium borate solution ($(NH_4)_3BO_3$, Wako Pure Chemical Industries, Ltd.) as shown in Figure 1. A platinum (Pt) pate was utilized as the cathode and then the ammonium borate solution was decomposed by the electric voltage of 10 V in 5 min. An oxidized layer was formed on the surface of the Nb anode and the color change from white to yellow was observed. The same procedures were repeated except that the applied voltages were changed from 5 to 100 V.

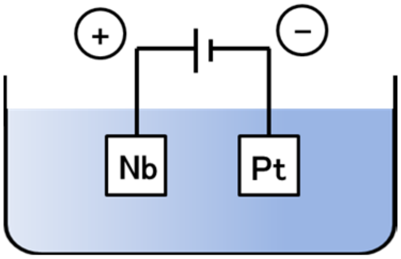

***Figure 1**. Schematic diagram showing the coloration of Nb films by electrodeposition in a 50 ml of a 5.0 w/w% ammonium borate solution*

The reflections of these Nb films as a function of incident light were measured, using a goniophotometer (JASCO V-670), in order to check the incident angle dependence of colors. In addition, in order to calculate the reflection and absorption peak wavelengths of colored Nb films with the reflective index and thickness of the Nb_2O_5 on Nb layers, the cross sectional views of the Nb films were observed using Focused ion beam (FIB, Hitachi FB-2000A) and Scanning electron microscopy (SEM, Hitachi S-4700 or S-4800 instrument).

2.2 Coloration and characterization of Ag films

Ag films prior to the color treatment were made on ca. 10 x 10 mm plastic plates by sliver mirror reaction using two head spry as described in the literature [6]. Typical procedures for coloring Ag films by sulfide solutions were carried out as follows: 4 pieces of Ag films on plastic board to tips of chopsticks were dipped in a 50 ml of a 1.0 w/w%, 50 °C lime sulfur as shown in Figure 2. The dipping was allowed to 5, 10, 15, and 20 sec. The pieces were then picked up, rinsed by de-ionized water, and dried in air.

The reflections of these Ag films as a function of incident light were measured and the cross sectional views of the Ag films were observed using the same procedures described for Nb films above.

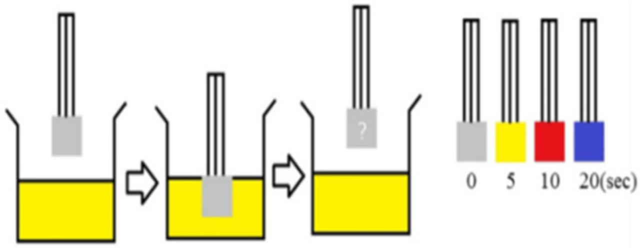

***Figure 2**. Schematic diagram showing the coloration of Ag films dipped in a 50 ml of a 1.0 w/w%, 50 °C lime sulfur solution*

3. Results and Discussion

3.1 Coloration and characterization of Ng films

Nb films oxidized by the anode oxidation are shown in Figure 3 with their preparation conditions. The surface of the Nb films turned various colors including yellow, purple, red, blue and green. In this preparation, we obtained different colors of Nb films as a function of the applied voltage. This result suggests that we can control the colors of Nb films by changing only the applied voltage.

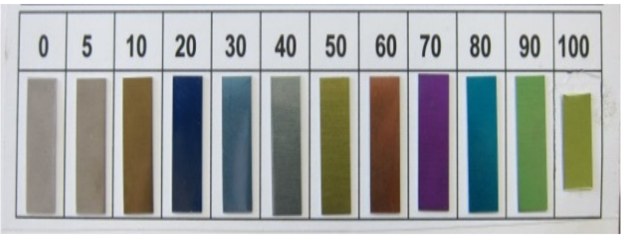

***Figure 3**. Color of original Nb film and Nb films oxidized by anode oxidation applied voltage of 5-100 V.*

Our goniophotometer studies of Nb films with changing the incident angle are presented in Figure 4 which shows the refraction spectra of Nb films as a function of the incident light angle. We found that the incident angle increases the refraction and/or absorption peak of reflection spectra shift to shorter wavelengths. These absorption shifts suggest the incident angle dependence of colors which is one of characteristics specific to thin film interference. Thin film interference is the phenomenon that occurs when incident light waves reflected by the upper and lower boundaries of a thin film interfere with one another to form a new wave. The interference is constructive when the optical path difference is equal to an integer multiple of the wavelength of light, λ. This condition can be expressed by the equation below;

$$2nd\cos\theta = m\lambda \qquad (1)$$

where, in this case, n is the reflective index of Nb_2O_5, d is the thickness of Nb_2O_5, θ is the angle of incidence of the light on the boundary between the Nb_2O_5 and Nb layers, m is an integer, and λ is the wavelength of light. This condition may change after considering possible phase shifts that occur upon reflection. This equation suggests that the color of the film is strongly dependent on the thickness of the Nb_2O_5 layer.

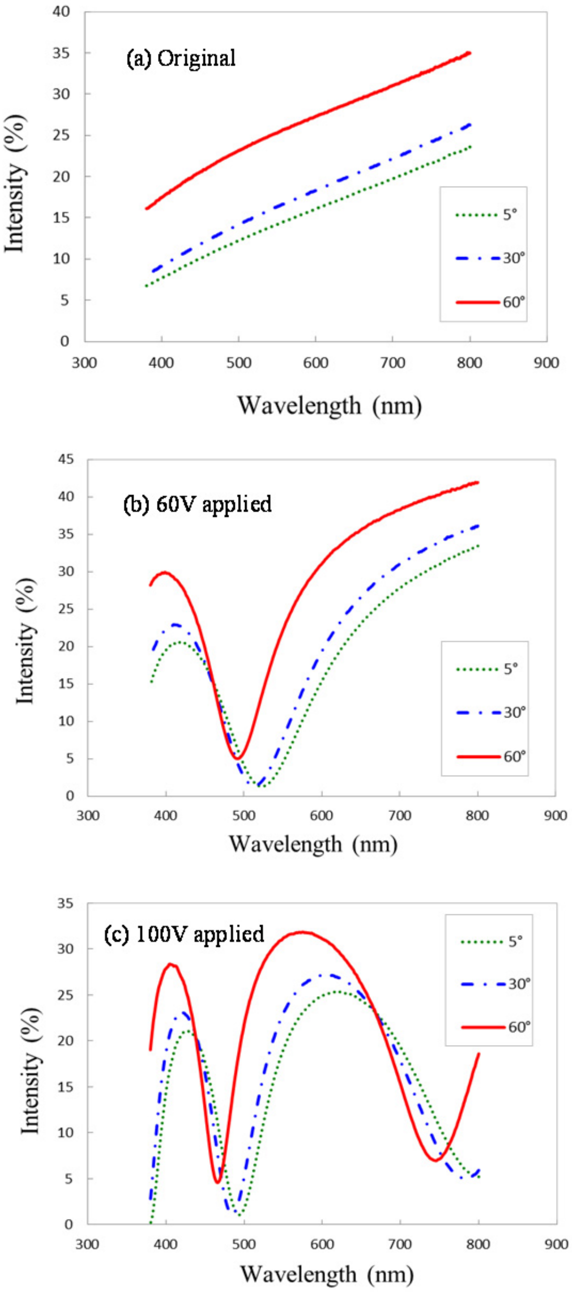

***Figure 4**. Refraction spectra of original Nb film and Nb films oxidized by anode oxidation applied voltage of 60 and 100 V as a function of the incident light angle of 5 °, 30 ° and 60 °*

The scanning electron micrograph depicted in Figure 5 is the cross sectional view of the green-colored Nb film applied 100 V. From the micrograph the thicknesses of Nb_2O_5 layer of the green-colored Nb film is estimated to be 246 nm. Plugging in the reflective index of Nb_2O_5 (n=2.5) and the estimated thickness of Nb_2O_5 layer above for equation (1), we calculated the refraction and absorption peaks of these samples. The difference of absorption peak wavelengths of Nb_2O_5 layer on Nb film between the experimental data by the goniophotometer and the calculated data with the reflective index and thickness of the Nb_2O_5 layers are presented in Figure 6. We found that the absorption peak wavelength of the green-colored Nb film applied 100 V experimentally observed using goniophotometer is reasonably in good agreement with the calculated data with the reflective index and thickness of the Nb_2O_5 layers.

From the results above, we confirmed that these Nb films exhibit their various colors because of the thin film interferences.

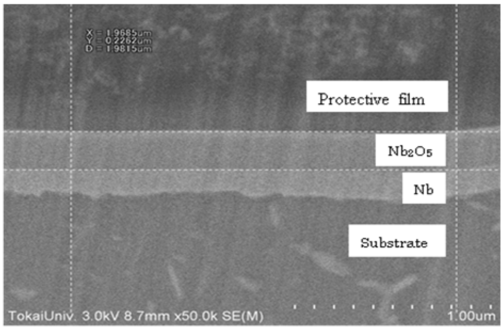

***Figure 5**. Cross sectional view of Nb film oxidized by anode oxidation applied voltage of 100 V*

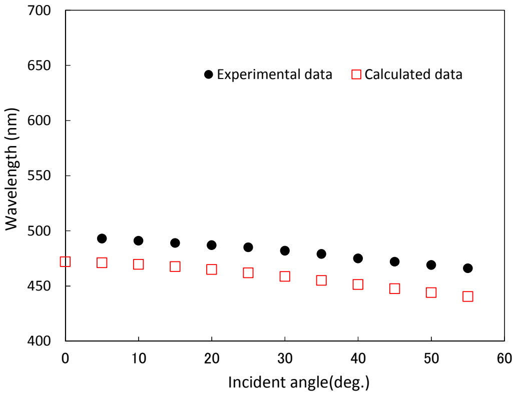

***Figure 6**. Difference of absorption peak wavelengths of Nb_2O_5 layer on Nb film between the experimental data by the goniophotometer and the calculated data with the reflective index and thickness of the Nb_2O_5 layer*

3.2 Coloration and characterization of Ag films

Ag films dipped in lime sulfur solution are shown in Figure 7 with their preparation conditions. The surface of the Ag films dipped in lime sulfur solution turned yellow, red, and blue respectively. In this preparation, we obtained different colors of Ag films as a function of the dipping time in a lime sulfur solution. This result suggests that we can control the colors of Ag films by changing only the dipping time in the lime sulfur solution.

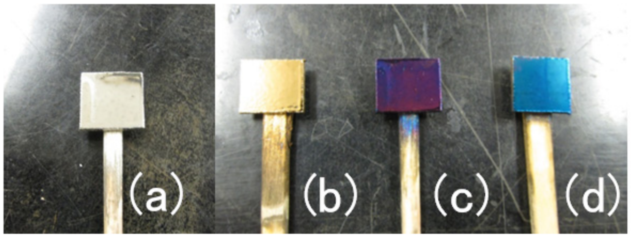

***Figure 7**. Color of original Ag film (a) and Ag films dipped (b) 5, (c) 10, (d) 20 sec in a 1.0 w/w%, 50 °C lime sulfur solution*

Our goniophotometer studies of Ag films with changing the incident angle are presented in Figure 8 which shows the refraction spectra of Ag films as a function of the incident light angle. We found that the incident angle increases the refraction and/or absorption peak of reflection spectra shift to shorter wavelengths. These absorption shifts suggest the incident angle dependence of colors which is one of characteristics specific to thin film interference.

The scanning electron micrographs depicted in Figure 9 are of cross sectional views of the yellow-colored Ag film and the blue-colored Ag film. From these micrographs the thicknesses of Ag_2S layers of the yellow-colored and the blue-colored Ag films are estimated to be 207 nm and 312 nm, respectively. Plugging in the reflective index of Ag_2S (n=2.9) and the estimated thickness of Ag_2S layers above for equation (1), we calculated the refraction and absorption peaks of these samples. The difference of absorption peak wavelengths of Ag_2S layer on Ag film between the experimental data by the goniophotometer and the calculated data with the reflective index and thickness of the Ag_2S layers are presented in Figure 10. We found that the absorption peak wavelengths of the yellow-colored and the blue-colored Ag films experimentally observed using goniophotometer are reasonably in good agreement with the calculated data with the reflective index and thickness of the Ag_2S layers.

From the results above, we conclude that these Ag films as well as Nb films exhibit their various colors because of the thin film interferences.

Finally, we note that these color-changeable Ag and Nb films have a number of potential applications including coating materials, imaging materials, and optical memories, since these films are easy to prepare, low cost, and applicable to a large area.

4. Conclusion

We confirmed that the color change of our Ag films comes from thin film interference as well as that of Nb film.

Acknowledgements

We would like to express our sincere gratitude to Dr. Kuroda of Kuroda Consulting Incorporated for our useful discussion. Mr. Miyamoto and Mr. Haraki of the Technical Service Coordination Office of Tokai University are thanked for their kind assistance with the SEM studies on the Ag/Nb films. This work is supported by JSPS KAKENHI Grant Number 24560892.

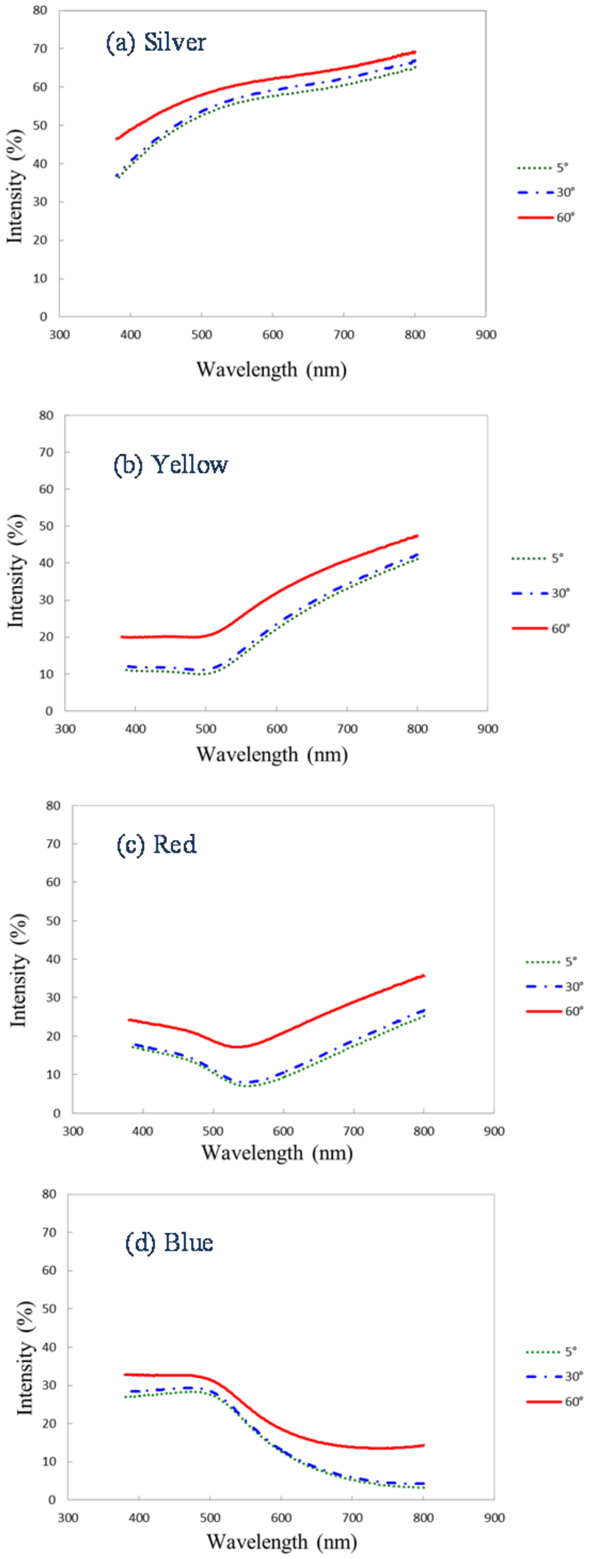

Figure 8 *Refraction spectra of (a) original Ag film and Ag films dipped (b) 5, (c) 10, (d) 20 sec in a 1.0 w/w%, 50 °C lime sulfur solution whose color is yellow, red and blue, respectively as a function of the incident light angle of 5 °, 30 ° and 60 °*

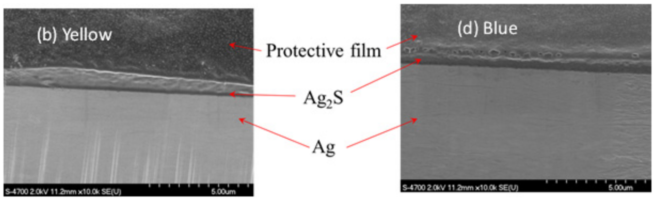

Figure 9*. Cross sectional views of Ag films dipped (b) 5, (d) 20 sec in a 1.0 w/w%, 50 °C lime sulfur solution whose color is yellow and blue using SEM*

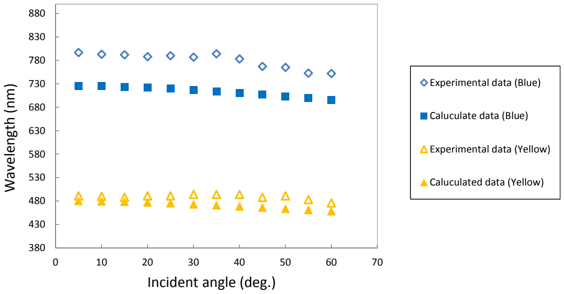

Figure 10*. Difference of absorption peak wavelengths of Ag_2S layer on Ag film between the experimental data by the goniophotometer and the calculated data with the reflective index and thickness of the Ag_2S layers*

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