

Analysis of Iodide and Bromide Profile in AgCl Cubic Crystal by TOF-SIMS

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Abstract

Quantitative analysis of depth profile of iodide and bromide ion compositions in AgCl cubic crystal by Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) has been established. The depth resolution is estimated to be ca. 2 nm by using well-defined multilayer thin film. Comparing the bulk compositions of halide ions obtained by ICP-MS method with halide compositions by TOF-SIMS, the surface composition of iodide and bromide were evaluated to be in the range of I:0-3.4 mol% and Br:0-50 mol%, respectively. The sputtering rate of AgCl with 15 keV DC ion beam of ⁶⁹Ga is estimated to be 2.2 nm/min by measuring the crater depth with AFM.

By repeating the sputtering of AgCl with ⁶⁹Ga ions and analyzing the surface composition of iodide and bromide with TOF-SIMS alternatively, it is shown that the depth profile depends on the doped halide ions. Iodide ion mainly exists at the surface of crystal and the concentration of iodide decreases gradually from the surface to the inside of the crystal. On the contrary, bromide ion exists only in a certain inner region crystal creating a Br-rich band, which we call the "Br-band". The depth of this "Br-band" is found to vary with addition timing of KBr in the AgCl crystal growth process.

Introduction

It is well known that the composition of surface layer of silver halide crystal is essential for the photographic properties such as sensitivity, stability of latent image and graininess. In recent years, the demand for high sensitivity of AgCl, used in color printing material, has grown rapidly. One method of obtaining high sensitivity of AgCl is to add small amount of iodide and/or bromide in the crystal. It is important to clarify the depth profile of halide ions doped in crystal to improve the high performance silver-halide emulsion. Some analytical techniques were reported that reveal the depth profile of halide ion in silver-halide crystal. Niedzwiecki and Tan reported that iodide was concentrated

at the surface of crystal by using Ion Scattering Spectroscopy (ISS) [1,2]. Geuens reported that it was possible to analyze depth profile of small amount of halide ion in the crystal by TOF-SIMS with Cs ion sputtering technique [3,4]. To acquire the accurate information about the depth profile by using ion-beam sputtering technique, it is important to ensure the depth resolution, the quantitative analysis of small amount of halogen at the surface of crystal and that no-damage is done to the crystal during sputtering process. The aims of this report are (1) to establish the analytical condition of measuring depth profile quantitatively and (2) to make clear the difference of depth profile between iodide and bromide in the cubic AgCl crystal.

Experimental

AgCl cubic crystal was prepared by double jet method with mixing AgNO₃ and NaCl to keep the silver ion concentration constant. KI and/or KBr of 0.1-0.3 mol% was added during the AgCl crystal growth process. Gelatin was removed from the AgCl emulsion by hydrolyzing enzyme washing and by centrifugal separation. The obtained AgCl crystals were spreaded on a silicon wafer and the shape of crystal was observed with SEM (Hitachi S-900). The AgBr_xCl_(1-x) (x = 0.1 to 0.5) sample with uniform composition, which was checked by X-ray diffraction method, was prepared by annealing crystals at 70 °C under argon gas for one month. AgCl thin film which was made by evaporation method (500 nm thickness) was used to estimate the sputtering rate of the ion gun. The depth of the crater generated by sputtering with ⁶⁹Ga ion beam was analyzed with SPI3800N (SII) AFM system. The compositions of iodide and bromide at the crystal surface were analyzed with TOF-SIMS (TRIFT II, Physical Electronics) and ESCA (ESCA5300, Ulvac Phi). Sample was cooled at -120 °C with liq.N₂. Liquid Metal Ion Gun (LMIG) of 15 keV ⁶⁹Ga was used both for sputtering process and surface analysis. The sputtering was operated with DC ion beam (ion current;600 pA) and the area of

sputtering was set to $240 \times 240 \mu\text{m}^2$. Surface analysis was operated with pulsed ^{69}Ga ion as the primary ion, 10 kHz repetition rate (ion current; 0.06 pA) and the analysis area was reduced to $60 \times 60 \mu\text{m}^2$ size. Charge accumulation during sputtering and measurement was compensated with low-energy electrons flooded on the entire area of sample.

Results and Discussions

Depth resolution of sputtering process

Photo.1 shows TEM image of the multilayer thin film consisted of Si layer (6 nm) and Ta layer (4 nm). This multilayered sample was sputtered with ^{69}Ga DC ion. Figure 1 shows the intensity of positive secondary ion for Si^+ (m/z 28) and $[\text{Ta}+\text{H}]^+$ (m/z 182). This profile shows a stack of bi-layers, each consisting of Silicon and Tantalum layer. The depth resolution was estimated to be 2 nm by comparing TOF-SIMS profile with TEM image.

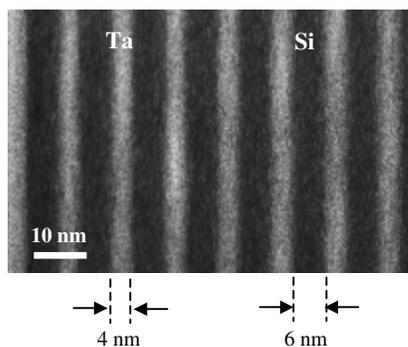


Photo.1 TEM image of the multilayer thin film

Sputtering rate of AgCl grains

Figure 2 shows the relationship between the sputtering time and the depth of crater measured by AFM. By using the linear relationship observed in the region between surface and 70 nm depth, it was estimated that AgCl was sputtered with 2.2 nm/min by the 15 keV DC ion beam of ^{69}Ga at -120°C .

SEM observation of Sample

Photo.2 shows the SEM image from the top view of the AgCl cubic crystal spread over the Si wafer. As each AgCl cubic crystals was oriented regularly on Si wafer, it is conceivable that only the uppermost surface area of AgCl crystal is being measured even though the area of TOF-SIMS measurement ($60 \times 60 \mu\text{m}^2$) was wider than the size of each crystal.

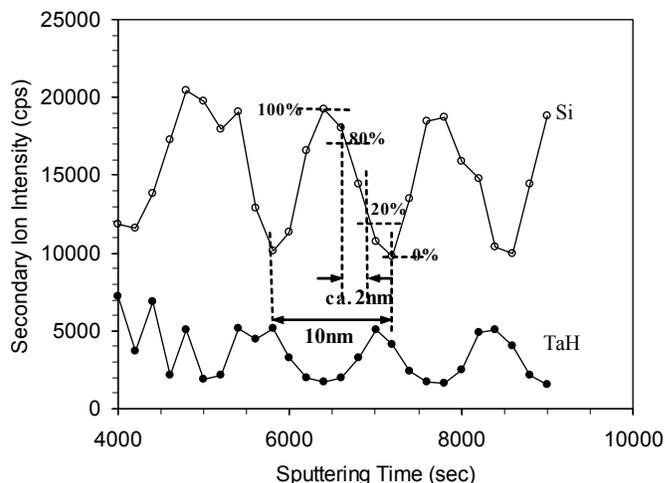


Figure 1 Profile of intensity of positive secondary ions for multilayer thin film

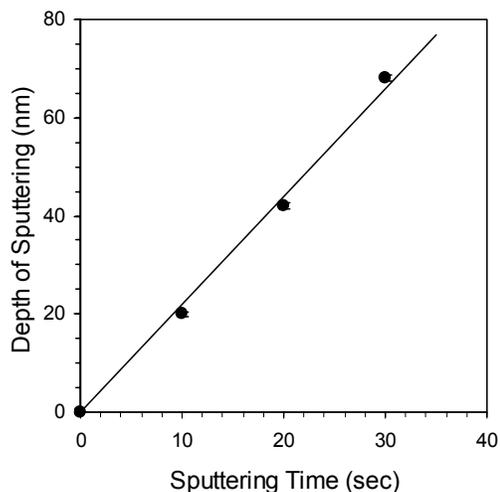


Figure 2 Sputtering rate of AgCl

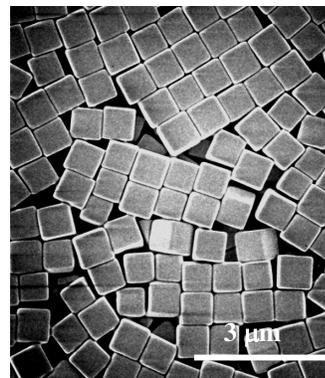


Photo.2 SEM image of the top view of AgCl crystals spread over Si wafer

Quantitative analysis of surface concentration of I and Br with TOF-SIMS

To avoid the saturation of Multi Channel Detector, ^{37}Cl was selected instead of ^{35}Cl which is the main isotope. To minimize the dead time after strong signal, the mass of ^{35}Cl was blanked by changing the voltage of the blanking plate in TOF-SIMS analyzer. Figure 3 shows the intensity ratio of bromide to total halide, and good relationship between ESCA ($\text{Br}/(\text{Br}+\text{Cl})$) and TOF-SIMS ($^{79}\text{Br}/(^{79}\text{Br}+^{37}\text{Cl})$). This result shows the possibility of quantitative analysis of surface bromide concentration with TOF-SIMS. The global bromide concentration in the $\text{AgBr}_x\text{Cl}_{(1-x)}$ crystal measured by ICP-MS correlated with the surface composition estimated by TOF-SIMS in the concentration of 0-50 mol% (Figure 4). In the case of iodide measurement, it was in the range of 0-3.4 mol%.

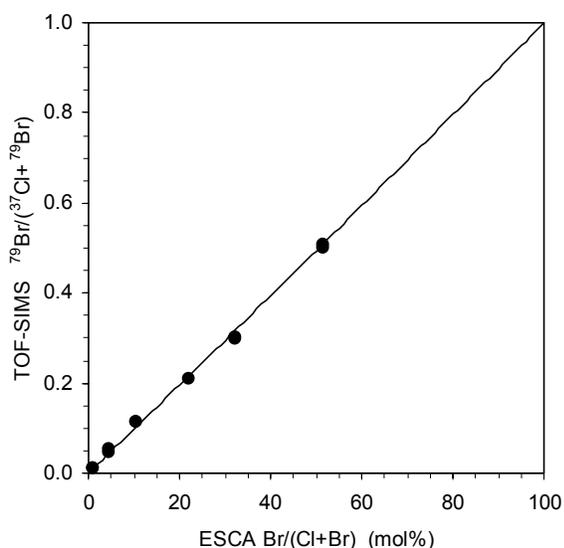


Figure 3 Relationship between the surface bromide concentration and the ratio of signal intensity of TOF-SIMS

After sputtering the homogeneous AgBrCl with ^{69}Ga DC ion beam, the new surface composition was evaluated with ESCA. Almost no change of surface composition was observed within $\pm 3\%$ accuracy. It became clear that no selective sputtering phenomenon for chloride and bromide was observed during ^{69}Ga DC ion beam sputtering process.

These data show that quantitative analysis of depth profile of iodide and bromide ion concentration in sub-micrometer size AgCl cubic crystal with TOF-SIMS was established using alternative sputtering of AgCl with DC ion beam of ^{69}Ga and analysis of surface concentration of iodide and bromide with TOF-SIMS.

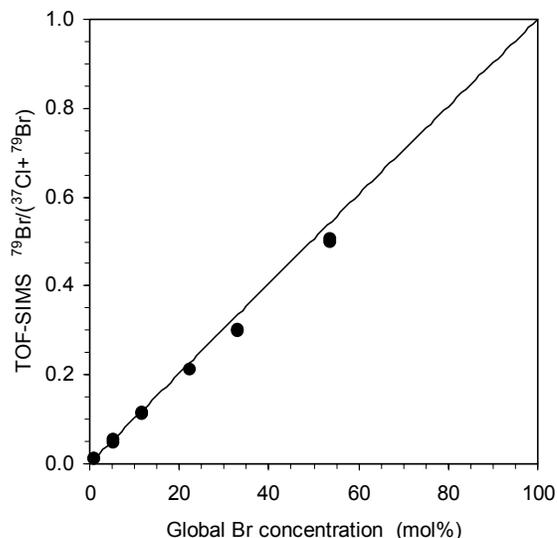


Figure 4 Relationship between the global bromide concentration of homogeneous AgBrCl and the ratio of signal intensity of TOF-SIMS

Depth profile of iodide and bromide in cubic AgCl crystal

Figure 5 shows the depth profile of iodide in cubic AgCl crystal with $0.7\ \mu\text{m}$ size in which KI was added at the point of 70 vol% crystal growth. It was clear that iodide concentration was the highest at the surface of the crystal and gradually decreased from the surface to inside of crystal. Figure 6 shows the bromide distribution in the crystal, in which KBr was added at the 70 vol% of crystal growth. The depth profile of bromide in the crystal was quite different from that of iodide. Bromide was concentrated about 3 times in the inner position of the crystal, and a bromide-rich layer, which we call Br-band, was observed. The position of Br-band depends on the timing of KBr addition in the crystal growth. It is easily estimated that iodide has the tendency to separate off to the surface of the AgCl crystal because of the low limit of solid-solution of iodide in AgCl .

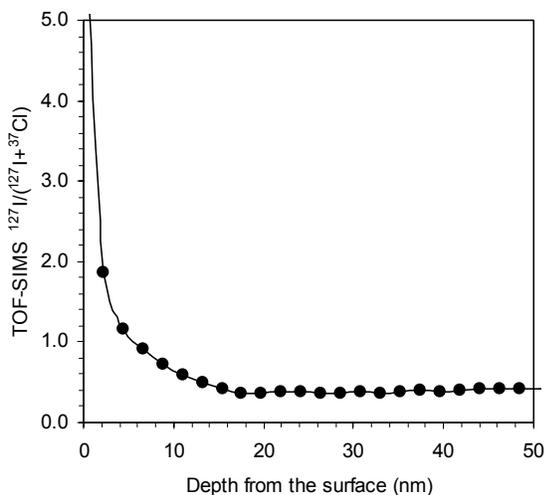


Figure 5 Depth profile of iodide ion in AgCl cubic crystal. KI was added at the time the crystal grew 70 vol% and global iodide concentration was 0.3 mol%.

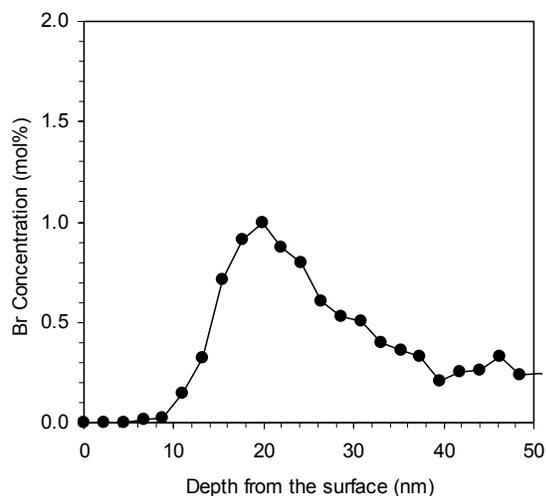


Figure 6 Depth profile of bromide ion concentration in AgCl cubic crystal. KBr was added at the time the crystal grew 70 vol% and global bromide concentration was 0.3 mol%.

Conclusion

Quantitative analysis method of depth profile of halide ion in AgCl cubic crystal was established by TOF-SIMS. It was revealed that the depth profile of iodide and bromide ion (global concentration is about 0.3 mol%) incorporated in the AgCl cubic crystal was quite different. Iodide ion was found to be at the surface of crystal and bromide ion had the tendency to exist in the inner region of crystal creating a Br-rich band.

References

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Biography

Toshihiko Maekawa received his master's degree in Polymer Chemistry from Waseda University at Tokyo in 1985. The same year and since then, he has worked in Research Laboratories at Fuji Photo Film Co., Ltd. in Minami-ashigara City. He has been engaged in the research of analytical chemistry.