In-Situ XAFS Analysis of Oxidation Process of Copper(I) Nitride Nanoparticle at Elevated Temperature

Marina Nakai[1], Toshiki Watanabe[1], Takashi Nakamura[2], Misaki Katayama[1], and Yasuhiro Inada[1]

1) *Department of Applied Chemistry, College of Life Sciences, Ritsumeikan University, 1-1-1 Noji-Higashi, Kusatsu 525-8577, Japan*
2) *Research Center for Compact Chemical System, National Institute of Advanced Industrial Science and Technology (AIST), 4-2-1 Nigatake, Miyaginoku, Sendai 983-8551, Japan*

1. Introduction

Copper nitride (Cu_3N) is an important semiconductor, which has a potential to be used as a high-speed integrated circuit material, and it is also applied as an optimal material for printed electronic devices. The flexible wiring of metallic Cu on a circuit board is possibly by the temperature-programmed reduction after spraying a suspension ink of Cu_3N. The similar treatment under the oxidative conditions generates the desired pattern made of copper oxides. The understandings on the oxidation process of Cu_3N are important to control the oxide product. In this study, *in-situ* XAFS measurements of the Cu species have been performed during the temperature-programmed oxidation (TPO) processes of Cu_3N.

2. Experimental

The Cu_3N samples were prepared by the liquid phase reduction method using copper(II) acetate monohydrate dissolved in 1-nonanol [1]. The solution was bubbled by ammonia gas (100 mL/min) and was heated at 190 ˚C to form the Cu_3N nanoparticle. The homogeneous precipitation method using urea was also applied to prepare Cu_3N. The 1-nonanol solution of copper(II) acetate containing urea was heated at 190 ˚C under the N_2 gas flow. The precipitated Cu_3N powder was filtered, washed by 1-nonanol for both preparation methods. The formation of Cu_3N was confirmed by the XRD measurements.

The *in-situ* XAFS measurements ware carried out in the transmission mode at BL-3 of the SR center (Ritsumeikan University) and BL-9C of the Photon Factory (KEK) at the vicinity of the Cu K edge during the TPO process. The temperature was elevated up to 600 ˚C with the increase velocity of 5 ºC/min under the oxidative quasi air atmosphere (20 % O_2 balanced by He).

3. Results and Discussion

The observed XANES spectral change is shown in Fig. 1 for the oxidation process of Cu_3N prepared using ammonia and urea as the nitrogen source. The initial spectra of Cu_3N were changed to that of CuO at the end of the TPO process for both samples. The appearance of some isosbestic points indicated that the intermediate species were not predominantly existed during the oxidation of the initial reactant, Cu_3N, to the final product, CuO.

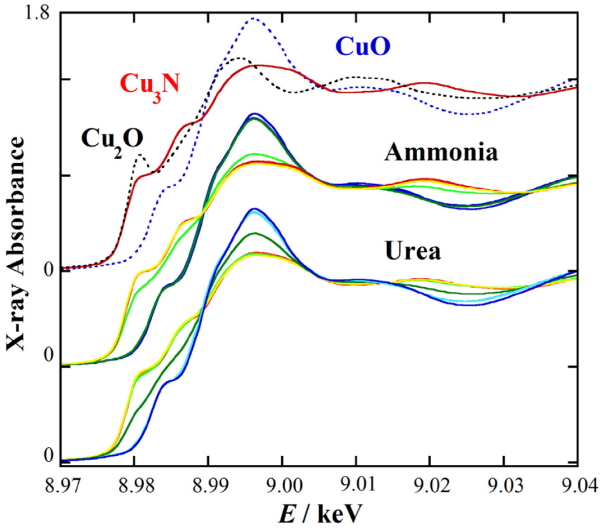

Fig. 1 XANES spectral change during the TPO process under the oxidative quasi air atmosphere.

Figure 2 shows the composition change as a function of temperature calculated by a linear combination analysis based on the XANES spectra in considering three components of Cu_3N, Cu_2O, and CuO. As mentioned above, the intermediate Cu_2O was found to be a minor component under the present TPO conditions, and was formed at *ca*. 200 ˚C with the maximum composition of 10 %. The fully oxidized product of CuO was formed at *ca*. 400 ˚C in the case of Cu_3N prepared under the ammonia gas flow. The slightly lower oxidation temperature of Cu_3N prepared by the homogeneous precipitation method suggests the smaller particle size, which was in agreement with the size difference estimated by the XRD measurements. The present research proposes the suitable oxidation condition of Cu_3N to obtain the CuO material.

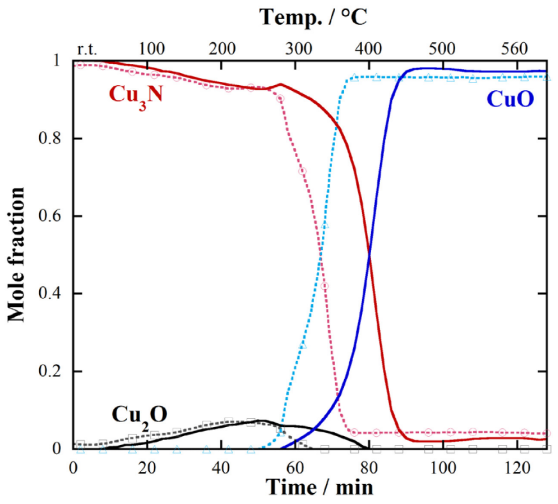

Fig. 2 Composition change as a function of temperature during the TPO process. The change of Cu_3N prepared using ammonia and urea was represented by solid and dotted line, respectively.

Reference

[1] T. Nakamura, H. Hayashi, T. Hanaoka, and T. Ebina, *Inorg. Chem.*, **53**, 710-715 (2014).