11B/2004G062

X-ray Absorption Near Edge Structure (XANES) Studies of Silver salt and its Photochemical Products

Takeshi Miyamoto[1], Hironobu Niimi[2], Wang-Jae Chun[2, 3], Yoshinori Kitajima[4], Hideyuki Sugawara[5], Tamotsu Inabe[5], and Toshio Naito[5, 6], Kiyotaka Asakura*[1, 3]
[1]Department of Quantuam Science and Engineering, Hokkaido Unversity 21-10,Sapporo,001-0021
[2]CREST JST, 21-10 Sapporo 001-0021
[3]CRC,Hokkaido University, 21-10, Sapporo,001-0021
[4]PF-IMSS-KEK, Oho1-1, Tsukuba,305-0801
[5]Division of Chemistry, Graduate School of Science, Hokkaido University, 10- 8, Sapporo, 060-0810.
[6]CRIS, Hokkaido University, 21-10, Sapporo, Hokkaido 001-0021

Introduction

A silver salt $Ag(DM)_2$ (DM=2,5-dimethyl-*N,N'*-dicyanoquionediimine) shows one dimensional(1D) metallic conductivity due to 1D π-electronic band of the DM anion column. This salt also shows photosensitivity; the conductivity dramatically changes from metallic to semiconducting and insulating ones only by UV-VIS light illumination under different conditions. This property can be utilized to fabricate 1D electronic devices directly by photolithography. Further investigation has revealed that four different kinds of product are created by the illumination of $Ag(DM)_2$. Their properties are summarized in Table1. We characterized the Ag chemical state by measuring Ag L_3-edge XANES spectra of pristine and four photochemical products of $Ag(DM)_2$, and proposed the photo-indcued conduction changing mechanism.

Experimental

XANES measurements were carried out at BL11B in a sample current mode. The sample powder was put on the conductive carbon tape and was loaded in a UHV chamber.

Result and discussion

Fig. 1 shows the L_3-edge XANES spectra of pristine $Ag(DM)_2$, its four photochemical products and Ag foil for reference. The spectrum shows that the photo products classify into two according to the Ag chemical state. α,β and γ gave similar spectra which showed a peak around 3352 eV. These peaks could be assigned to a 2p → 4d dipole transition. Since the Ag^+ in α was usually thought to be d^{10}, the d vacancy might be created by the back-donation from Ag^+ to DM^-. The occurrence of the edge peak in α, β, and γ meant that the Ag should have the bond with ligands and be cationic. β almost the same chemical state and structure of α. But γ is amorphous state from XRD. The changing conductivity mechanism of γ is as follows. The energy brought in through the photoexcitation is used to break the stacking structure of the DM column. Consequently, the conduction path is disrupted.

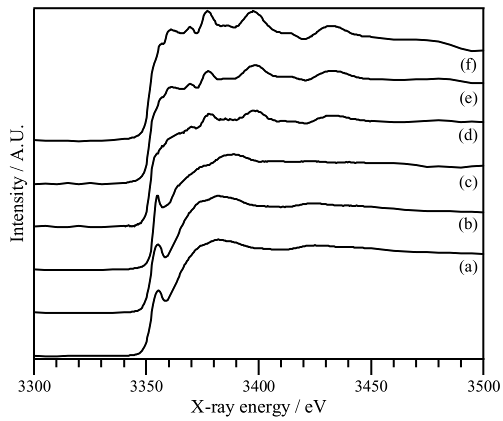

Fig. 1. Normalized Ag L_3-edge XANES spectra for $Ag(DM)_2$ and its light induced products. (a)α, (b)β, (c)γ, (d)δ, (e)ε and (f) silver foil.

On the other hand, δ and ε gave the same spectra as that of Ag foil, indicating the formation of Ag metal in δ and ε due to the redox reactions between Ag^+ and DM^-. DM molecules were neutralized and sublimated and hence the conductivity was lost in δ.

These findings are important to control the photoprocesses and to create a new device from $Ag(DM)_2$.

References

1. A. Aumüller et al. Angew. Chem. Int. Ed. Engl. 25, 740 (1986)
2. T. Naito et al. Adv. Mater. 16, 1786 (2004)
*askr@cat.hokuai.ac.jp

Table 1. The properties of the pristine $Ag(DM)_2$ and photo-induced products β, γ, δ, and ε.

product	α (pristine)	β	γ	δ	ε
color	Black	Black	Brown	Black	Silver White
appearance	Needle	Needle	Needle	powder	powder
stoichiometry [DM/Ag]	2	2	2	1.5	~ 0
XRD	$Ag(DM)_2$	$Ag(DM)_2$	amorphous	Ag foil	Ag foil
conductivity	metallic	semiconducting	Insulating	Insulating	metallic