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Reduction Reaction Analysis of Nanoparticle Copper Oxide by Formic Acid

Masahisa Fujino[1], Masatake Akaike[1], Naoya Matsuoka[1], and Tadatomo Suga[1]

[1]Univ. of Tokyo
7-3-1 Hongo, Bunkyo, Tokyo 113-8656 Japan
Phone: +81-3-5841-6494 Email: fujino.masahisa@su.t.u-tokyo.ac.jp

Abstract

Copper is one of the key materials of electronics devices recent days. In this research, we analyzed the reduction reaction of oxide copper by formic acid with Pt catalyst by electron spin resonance analysis and thermal gravimetry analysis. As result, formic acid is decomposed and radical hydrogen was generated under 200 °C, and the radical hydrogen generation mount was increased by adding Pt catalyst. Moreover, both copper (I) oxide and copper (II) oxide start to be decomposed from around 200 °C. and were decomposed completely at 400 °C. And also Pt catalyst decreases temperature of the oxide copper reduction. Herewith, it is considered that the electronics devices using copper can be assembled more effectively.

1. Introduction

In recent years, copper is progressing application to electronic devices because of its high electrical and thermal conductivity, electromigration resistance characteristics, and so on. In particular, wiring materials and electrodes as most significant application for copper with these properties. On the other hand, the oxide layer on the surface of copper wires and electrodes prevents easy assembling with reliable contact. Therefore, removal of oxide layer on copper surface is still main issue for low contact resistivity especially miniaturization of pitch size.

The methods of oxide layer removal on copper surface include as follow; hydrogen reduction method using hydrogen gas[1], hydrogen plasma reduction method[2], an organic acid wet process[3], the formic acid gas dry process[4], and so on. The hydrogen reduction method is by exposing the substrate containing copper to hydrogen gas more than 350 °C, in order to reduce copper oxide and to remove oxide layer on the copper surface. On the other hand, in the organic acid wet process, a copper oxide layer is removed by applying or immersing the organic acid solution diluted at room temperature. Since both methods damage to the other part of copper substrate by using the high-temperature environment or acid-containing solution, it is considered that formic acid gas dry process should be suitable for copper oxide film removal method at present. In the applied formic acid gas dry process, a copper oxide layer is removed by formic acid gas around 200 °C[5].

In this study, in order to analyze the reduction reaction of the copper oxide of formic acid gas in detail, copper oxide nanoparticles were prepared for expansion of reaction area of specimens, then electron spin resonance (ESR) analysis, thermal gravimetry (TG) analysis and quadrupole mass spectrometry (QMS) was performed.

2. Experimental Procedure

At first, the ESR analysis of formic gas reaction was performed as follow: Formic gas with Ar gas as flow gas was flowed through Pt catalyst, and reacted gas was dissolved into 5,5-dimethyl-1-pyrroline N-oxide (DMPO); then the DMPO was analyzed by ESR to detect the react gas from formic acid.

We also performed TG and QMS analysis of reduction reaction of oxide copper by formic acid. We prepared copper (II) oxide specimen as copper (II) oxide nanoparticles (grain diameter with 40–80 nm) from Ionic Liquid Technologies GmbH, Germany. The nanoparticles were set on the balance in the TG forge, and the formic acid gas with Ar gas was flowed into the TG forge. The reaction of the nanoparticle with formic gas was analyzed by TG, and the reacted gas was analyzed by QMS simultaneously. The apparatus setting of these analyses was shown in Fig. 1. In this TG/QMS analysis, not only copper (II) oxide but also copper (I) oxide which was produced from copper (II) oxide by annealing in vacuum around 800 °C was analyzed. Also the catalyst condition is one of the parameters by using Al cup as with non-catalyst condition, or Pt cup as with catalyst condition.

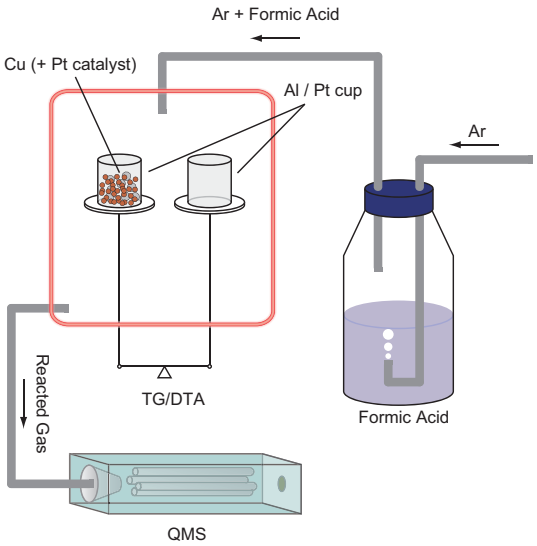

Figure 1 A schema of TG/QMS analysis setting.

3. Experimental Results

The ESR spectra of reacted formic acid with Pt catalyst at room temperature and 200 °C shows in Fig. 2.

These spectra with seven spikes from 3450 to 3520 G correspond to radical hydrogen. Therefore, radical hydrogen was generated by formic gas reacted to Pt catalyst, and it was generated much more at 200 °C.

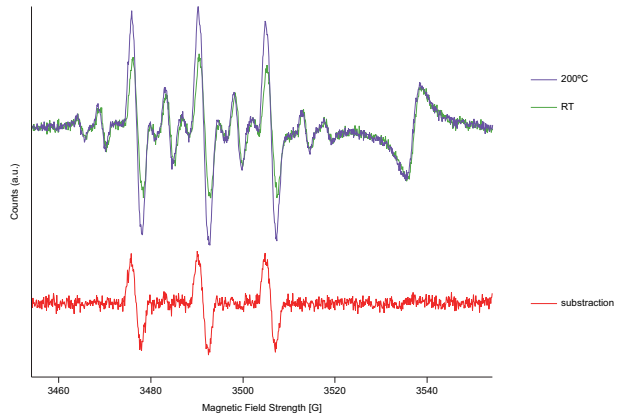

Figure 2 ESR spectra at 200 °C and room temperature.

The measurement results of the TG of copper (II) oxide and copper (I) oxide shows in Fig. 3. TG of Copper (II) oxide is about -20% at 350 °C and later, on the other hand, TG of copper (I) oxide is about -11% at 450 °C, It has become considered to reduction to copper to be -20.2% and -11.18% is completed in the respective theoretical values. In addition, although TG immediately after the start of the measurement around 150 °C has been increased by about 2–8%, formic acid from it and to stop the supply of formic acid continues to hold to 150 °C the value in QMS decreases each be adsorbed on the nanoparticles became apparent. Comparing the results of the TG of Al/Pt cup, Using Pt catalyst has been completely reduced to copper from both copper (II) oxide and copper (I) oxide at lower temperature than without catalyst. Moreover, determined the activation energy using Arrhenius plot from the rate of temperature increase, it is confirmed that Pt catalyst has decreased activation energy.

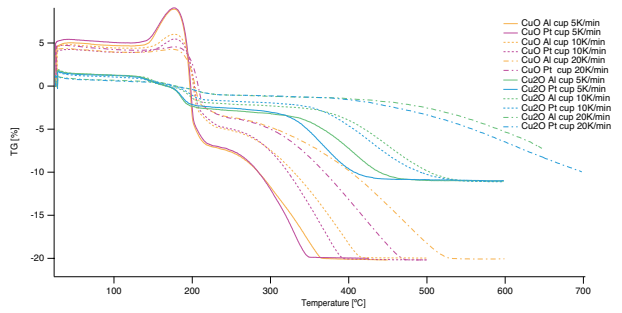

Figure 3 TG profiles of copper (II) oxide and copper (I) oxide using Al cup or Pt cup at the rate of temperature increase with 5 K/min, 10 K/min, 20 K/min

Further, QMS result for the generation of hydrogen gas during TG analysis shows in Fig. 4. It shows that adsorbed formic acid gas leaving from the copper oxide surface around 200 °C, then oxide copper oxide are reduced and hydrogen gas was generated during reduction process. According to the ESR result, it is considered that reduction reaction of copper oxide around 200 °C to be greater contribution of hydrogen radicals.

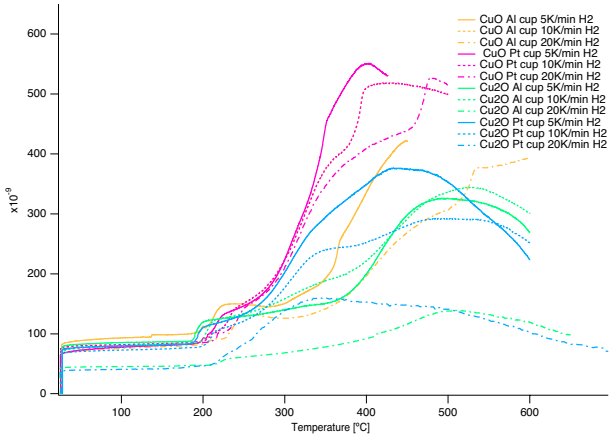

Figure 4 Generation of hydrogen gas by QMS during TG analysis of copper (II) oxide and copper (I) oxide using Al cup or Pt cup at the rate of temperature increase with 5 K/min, 10 K/min, 20 K/min.

4. Conclusion

The reduction reaction of copper oxide by formic acid gas precisely using ESR, TG, and QMS analysis. The reduction of copper (II) oxide and copper oxide (I) by formic acid gas starts from around 200 °C and it is completely reduced to copper at 400 °C or more. Pt catalyst reduces the activation energy of reduction and the reduction temperature can be decreased. Moreover, the two-step reduction reaction was observed that one is the reduction by absorbed formic acid around 200 °C and the other is that by the gas generated by the decomposition of formic acid gas more than 200 °C.

Acknowledgement

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