Microelectronic Engineering 141 (2015) 184–187

Contents lists available at ScienceDirect

Microelectronic Engineering

journal homepage: www.elsevier.com/locate/mee

Formation of zinc oxide thin film using supercritical fluids and its application in fabricating a reliable Cu/glass stack

Mitsuhiro Watanabe *, Shigeaki Tamekuni, Eiichi Kondoh

Interdisciplinary Graduate School of Medicine and Engineering, University of Yamanashi, 4-3-11 Takeda, Kofu, Yamanashi 400-8511, Japan

A R T I C L E I N F O

Article history:
Received 29 October 2014
Received in revised form 11 March 2015
Accepted 18 March 2015
Available online 25 March 2015

Keywords:
Supercritical fluid
ZnO films
Adhesion
Cu/glass structure

A B S T R A C T

This paper demonstrates zinc oxide (ZnO) film formation by using supercritical fluid chemical deposition and the application of the ZnO films in improving the adhesion of Cu/glass stacks. Bis(2-methoxy-6-methyl-3,5-heptanedionate)zinc(II) was used as a precursor, and the deposition was carried out at different oxygen contents and temperatures. When oxygen content was high and/or deposition temperature was high, white polycrystalline ZnO films were deposited; otherwise, the films were brown and had a higher carbon content. XPS analyses revealed that the white ZnO films had less carbon contamination. A significant improvement in the adhesion of the Cu/glass stacks was observed when the fabricated ZnO film was inserted between Cu and glass.

1. Introduction

Reliable and high-precision Cu/glass stacks are particularly desirable for microelectromechanical systems (MEMS) and packaging technologies. One solution for improving the adhesion strength of Cu/glass stacks is to form adhesion layers between the Cu films and the glass substrate. Many studies have shown that a strong adhesion layer is formed at the interface by high-temperature annealing when a Cu alloy is used instead of pure Cu [1–4]. High-temperature annealing generally requires a long annealing time for interfacial reactions. It is important to reduce the temperature and process time in order to reduce the thermal budget and fabrication cost. Therefore, the room-temperature formation of an adhesion layer is desirable.

Previously, we reported the room-temperature formation of an extremely thin intermixing layer at the Cu/glass interface. This layer was formed by doping the glass surface with Zn followed by noble metal catalyzation [5], and this intermixing layer significantly improved the adhesion at the Cu/glass interface. The fabrication process is shown in Fig. 1. This process is simple and allows conventional electroless Cu plating or any other common Cu deposition methods, such as sputtering, to be used. The key in this process is the combination of Zn doping and noble metal catalyzation, which accelerates atomic intermixing at the Cu/glass interface. For obtaining the Zn-doped glass surface, annealing of the ZnO/glass stack during or after ZnO deposition was effective treatment [5].

Our concern is to apply this process to the MEMS metallization, particularly for the fabrication of through-hole Cu interconnections embedded in glass substrates. This structure is used in glass interposers for large-scale integration (LSI) packaging, which compromise the differences in electrode pitch size between the upper LSI chips and the lower circuit. The through-holes have a high aspect ratio (HAR) to increase the interconnect density. Therefore, in applying our metallization method, it is necessary to deposit ZnO films on the sidewalls of the HAR nanostructures. Conventional deposition techniques, such as electrochemical deposition, physical vapor deposition, and chemical vapor deposition, are inappropriate because of their poor step coverage and/or low deposition rate.

Supercritical fluid chemical deposition (SFCD) is a technique for depositing thin films and particles through thermochemical reactions. A supercritical fluid is a state that exists above the critical point of a substance (CO_2: 7.38 MPa, 31.2 °C [6]) and has unique properties, such as zero surface tension, excellent diffusivity, and high solvent capability. These unique properties make supercritical fluids a promising medium for delivering reactant molecules to surfaces that have complex micro/nanosized structures. Namely, SFCD is an effective method for depositing thin films on the sidewalls of the HAR through-holes [7–11]. ZnO deposition using SFCD has been performed extensively nanoparticle formation [12–14], whereas there are few studies of thin film formation [15]. In the present study, we studied the deposition of ZnO films using bis(2-methoxy-6-methyl-3,5-heptanedionate)zinc(II)

* Corresponding author.
E-mail address: mitsuhirow@yamanashi.ac.jp (M. Watanabe).

http://dx.doi.org/10.1016/j.mee.2015.03.031
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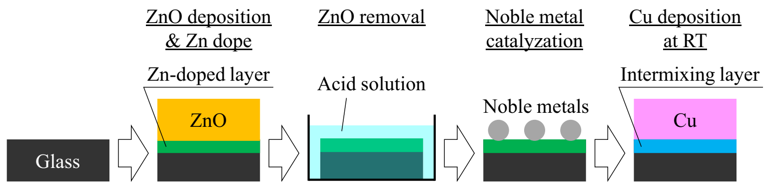

Fig. 1. Schematic diagrams of process for high-adhesion Cu/glass stack. RT means room temperature.

(Zn-MOPD, $Zn(C_9H_{15}O_3)_2$) as a precursor. In addition, we investigated whether the SFCD-ZnO films improve the adhesion of Cu/glass stacks.

2. Experimental procedure

A schematic diagram of the batch reaction system used in this study is shown in Fig. 2. Borosilicate glass plates were used as the substrate and Zn-MOPD was used as the precursor. Zn-MOPD is a brown liquid at room temperature. The precursor and glass substrate were placed in the reactor cell (2 ml). The cell was filled with gaseous oxygen, and liquid CO_2 was added to a pressure of 10 MPa. Namely, amount of CO_2 was fixed at 8.9×10^{-3} mol. The cell was then heated to the target temperature and the temperature was held for a fixed duration (20 min), followed by depressurization and cooling. The standard deposition conditions were a deposition temperature of 350 °C, an oxygen content of 9.4×10^{-4} mol, and a precursor concentration of 2.5×10^{-5} mol. The deposition temperature, oxygen content, and precursor content were changed from 200 to 350 °C, from 0.0 to 9.4×10^{-4} mol, and from 2.5×10^{-6} to 2.5×10^{-5} mol, respectively. After deposition, the films were characterized with X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). XPS depth analyses were performed by using Ar ion etching.

After depositing SFCD-ZnO, glass metallization was performed (Fig. 1) and the adhesion strength of the Cu/glass stacks was evaluated. For doping the glass surface with Zn, the SFCD-ZnO/glass stacks were annealed under Ar at 600 °C for 60 min. The ZnO films were removed from the glass substrate by dipping the stacks in an acid solution. Afterward, Pt particles were deposited on the substrate surface by sputtering. Finally, Cu films were sputtered to a thickness of 50 nm with no intentional substrate heating or cooling. These deposition conditions are our standard for obtaining high adhesion [5]. The adhesion strength was evaluated with a micro-scratch tester (Rhesca CSR-2000) following Japanese Industrial Standard R3255 specifications [16], where the load applied to the horizontally vibrating stylus was increased continuously with the traveling displacement of the stylus. The critical adhesion strength was defined as the applied load at which the delamination occurred. The delamination position was determined by observing the scratch mark using optical microscopy. Five different positions were tested for each sample.

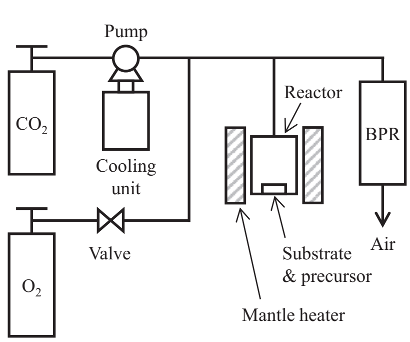

Fig. 2. Schematic diagram of SFCD apparatus.

3. Results and discussion

3.1. Deposition conditions and film characterization

Fig. 3 shows typical digital camera photographs of the deposited films. Depending on the deposition conditions, white or brown films were deposited. White films were obtained at higher deposition temperatures and high oxygen content. The specimen shown in Fig. 3(a) was obtained at 350 °C and 4.7×10^{-4} mol oxygen. In contrast, brown films were deposited at temperatures below 300 °C and at oxygen contents below 2.8×10^{-4} mol [Fig. 3(b)]. The precursor content did not affect the color of the deposited films, and white films were always deposited at a temperature of 350 °C and an oxygen content of 9.4×10^{-4} mol throughout our experiments.

The white and brown films were analyzed by XRD using Cu Kα radiation, and typical XRD patterns are shown in Fig. 4. A strong broad peak, which is located at smaller angles, arises from the amorphous structure of the glass substrate. Clear ZnO 100 ($2\theta = 32.18°$), 002 ($2\theta = 34.80°$), 101 ($2\theta = 36.66°$), 102 ($2\theta = 47.80°$), 110 ($2\theta = 57.00°$), and 103 ($2\theta = 63.18°$) reflections were observed in both the patterns, indicating that both the white and the brown films were polycrystalline ZnO. The full width at half-maximum values of these peaks obtained from the white films were smaller than those of the brown films, indicating that the white films had better crystallinity than the brown films.

Fig. 5 shows typical XPS depth spectra of Zn $2p_{3/2}$, O 1s, and C 1s core levels obtained from (a) the white and (b) brown ZnO films. The spectra are listed from the maximum depth (top spectrum) to the surface (bottom spectrum). At the surface, for both films, Zn, O, and C were detected, indicating that the surfaces of both ZnO films were contaminated with carbon and/or oxygen from the air. In the white ZnO films (Fig. 5(a)), the Zn and O peaks were stronger and clearer and the C peak intensity was extremely low. In the brown ZnO films (Fig. 5(b)), no energy shift in Zn peaks was observed up to the maximum depth. The intensities of the O peaks decreased as the etching depth increased, although the peaks did not disappear. Strong C peaks were observed in the film. The carbon contamination was assumed to degrade the crystallinity of ZnO, which agrees with the XRD results. These XPS results indicate that the white ZnO films contain less carbon contamination, more oxygen, and are better quality than the brown ZnO films.

The XRD and XPS results show that the brown ZnO films have the same crystal structure as ZnO, although they are contaminated with carbon. These films were deposited at temperatures of less than 300 °C. Metalorganic chemical vapor deposition (MOCVD) of ZnO films from Zn-MOPD has previously been performed in a temperature range of 400–600 °C [17,18]. The decomposition of Zn-MOPD was insufficient at 300 °C, and the unreacted or partially unreacted precursor was incorporated in the film, which resulted in the coloration of the film. This also means that Zn-MOPD is well decomposed and oxidized in supercritical CO_2 fluid at a higher