Journal of
Nanoscience and Nanotechnology
Vol. 11, 7322–7326, 2011

Surface Modification of Carbon Post Arrays by Atomic Layer Deposition of ZnO Film

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The applicability of atomic layer deposition (ALD) process to the carbon microelectromechanical system technology was studied for a surface modification method of the carbon post electrodes. A conformal coating of the ALD-ZnO film was successfully demonstrated on the carbon post arrays which were fabricated by the traditional photolithography and subsequent two-step pyrolysis. A significant Zn diffusion into the underlying carbon posts was observed during the ALD process. The addition of a sputter-deposited ZnO interfacial layer efficiently blocked the Zn diffusion without altering the microstructure and surface morphology of the ALD-ZnO film.

Keywords: Carbon Microelectromechanical System, Atomic Layer Deposition, Zinc Oxide, Pyrolysis.

1. INTRODUCTION

Recently, the carbon microelectromechanical system (C-MEMS) technology, which is based upon the conductive glassy carbon materials, has been widely investigated in many possible application areas, such as DNA detection,[1] glucose sensors,[2] Li ion batteries,[3] three-dimensional electrodes for dielectrophoresis,[4] etc. In the C-MEMS technology, the conversion of an epoxy-based, negative tone photoresist (PR) to conducting carbon is achieved by a pyrolysis process after photolithography.[1–4] Since the carbon post arrays are conductive and significantly increase the surface-to-volume ratio with their three-dimensional architecture, the improvement of sensing performances can be expected, in which the collection of charge carriers is important. In addition, various high aspect ratio structures are promising as a template for other nano-device applications at the interface of nano-scale materials and micro-scale devices. For exploring these, methods for surface modification are required and, especially, a dry process with controllable reaction variables is highly desirable for batch micro-fabrication.

The atomic layer deposition (ALD) method due to its nature of controlled processes with a capability of nearly perfect step coverage adequately satisfies all these requirements[5] and, therefore, is selected for the surface modification of the carbon post arrays in this work. ZnO film was selected among many metal oxides due to its wide applications in semiconductor devices and sensors,[6] and well-known chemical components and structural properties optimized for ALD process.

2. EXPERIMENTAL DETAILS

2.1. Fabrication of Carbon Post Arrays

As a bottom electrode, Pt (300 nm)/Ti (20 nm) was deposited by an electron beam evaporation on SiO_2/Si substrate. For the patterning of the PR post arrays, SU-8 2050 (Microchem Corp.), was spin-coated with a thickness of 80~90 μm and baked at 65 °C and 95 °C sequentially. A photomask that contains circular patterns in an array format was used for UV exposure. The PR post array pattern was completed after a post-exposure bake and a development process.

The PR-derived C-MEMS architecture was obtained by a two-step pyrolysis process established by Wang et al. in an open-end quartz-tube furnace.[3,7] The first pyrolysis step consists of heating at 350 °C for 30 min and ramping up the temperature to 900 °C in a nitrogen atmosphere. After reaching 900 °C, the atmosphere was changed to a forming gas (5% H_2/95% N_2). For the second pyrolysis step, the samples were kept for 1 hr and then cooled down to a room temperature in a nitrogen atmosphere.

2.2. ALD-ZnO Deposition and Characterization

On the carbon post arrays fabricated via the pyrolysis process, ZnO films were deposited by ALD process at

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1533-4880/2011/11/7322/005 doi:10.1166/jnn.2011.4827

150 °C with diethyl zinc [DEZn, $((C_2H_5)_2Zn)$] and H_2O as metal and oxidant precursors, respectively. The thickness of the ZnO film monitored on a bare-Si wafer was ∼40 nm with a deposition rate of ∼0.2 nm/cycle. In some samples, a 10 nm-thick, sputter-deposited ZnO film was inserted between the carbon post and ALD-ZnO layers for prevention of Zn diffusion into the underlying carbon layer, which was detected during the analysis of ALD-ZnO/carbon post samples. The interfacial ZnO layer was deposited using a RF magnetron sputtering system. After the initial deposition of the interfacial ZnO layer, an identical ALD-ZnO process was carried out.

In order to inspect the post arrays before and after the pyrolysis, scanning electron microscopy (SEM) was used. For detailed microstructural and interfacial analysis of the ZnO layers with the underlying carbon posts, cross-sectional transmission electron microscopy (TEM) samples were made by a focused ion beam (FIB) system. The samples were observed by a TEM system equipped with energy-dispersive X-ray spectroscopy (EDS). Furthermore, surface morphologies of the ALD-ZnO films on the carbon posts were characterized by SEM and atomic force microscopy (AFM).

3. RESULTS AND DISCUSSION

In order to prepare the carbon post arrays, first, PR post arrays with various aspect ratios were fabricated on the $Pt/Ti/SiO_2/Si$ substrate. Figure 1(a) shows a patterned array of PR posts of which individual diameter is 50 μm and the aspect ratio is 1.8. As shown in Figure 1(b), after the pyrolysis process, carbon post arrays which preserve the initial PR shapes were obtained without any adhesion problem. During the pyrolysis process, there was about 50% dimensional shrinkage in diameter and height of the carbon posts. A tapered shape was observed at the bottom region of the carbon post, which may originate from the initial strong adhesion between the PR and substrate[8] and/or the PR flow during the high temperature pyrolysis process.

When an ALD-coated ZnO film was observed by TEM, the cross-sectional image of Figure 2(a) clearly revealed that the ZnO film was uniformly deposited on the amorphous carbon post. The thickness of the ALD-ZnO film on top region of the carbon post was measured at ∼55 nm (Fig. 2(a)), somewhat higher than that on the bare-Si which was used as a monitoring wafer. It is known that the ALD growth rate is strongly dependent on the substrate surface condition.[9] According to the separate TEM analysis of the ALD-ZnO film on the sidewall region of the carbon posts (inset of Fig. 2(a)), the surface modification of the carbon posts by the ALD-ZnO process resulted in a conformal coating of ZnO film, exhibiting an excellent step coverage of >95% on the carbon post arrays.

According to the selected area electron diffraction pattern (SADP) obtained from the ZnO film (Fig. 2(c)), the ALD-grown ZnO film was observed to have a typical hexagonal phase. One interesting observation in the TEM images of the interface between the ALD-ZnO film and amorphous carbon (Figs. 2(a and b)) is an appearance of a broad region with alternating contrasts from the surface of the carbon layer and inward, implying a possible diffusion of Zn atoms. In order to confirm the interfacial inter-diffusion, an EDS line scan of Zn atoms was performed on the TEM sample across the ZnO and carbon interface as shown in Figure 3(a). A significant amount of Zn diffusion into the underlying carbon layer was observed almost down to ∼250 nm, which is believed to be a main origin for the contrast variation observed in the TEM images. Since the samples were not heat-treated after the ALD-ZnO deposition, it is possible that the Zn diffusion would have occurred during the ALD process at 150 °C. Although the ALD process temperature is considered to be quite low to initiate a significant amount of solid-state intermixing, the carbon post fabricated through a pyrolysis process has an amorphous phase with a disordered structure[8] and, thereby, may have facilitated a fast diffusion of the Zn atoms dissociated from the DEZn precursor. This kind of Zn diffusion process may proceed in a percolative way, which is well reflected in the observed TEM images (see Figs. 2(a and b)).

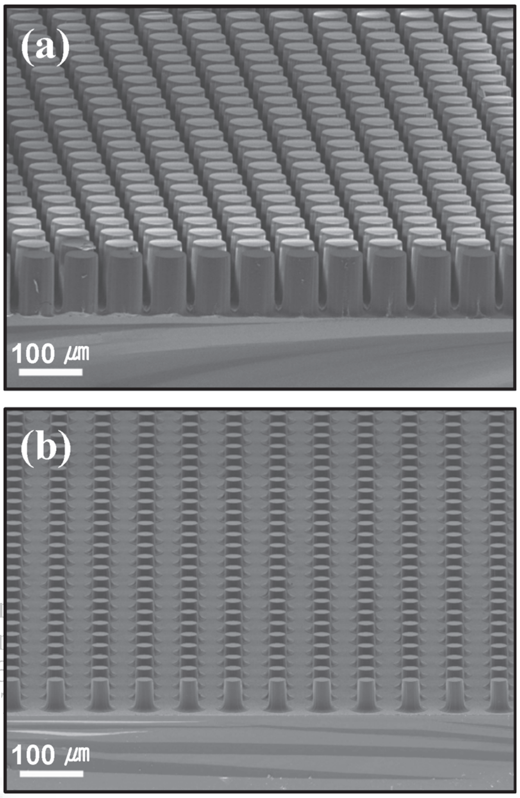

Fig. 1. Tilted SEM images showing PR post arrays (a) before and (b) after pyrolysis process.

In order to avoid the severe infiltration of Zn atoms into the underlying carbon posts, a sputter-deposited ZnO

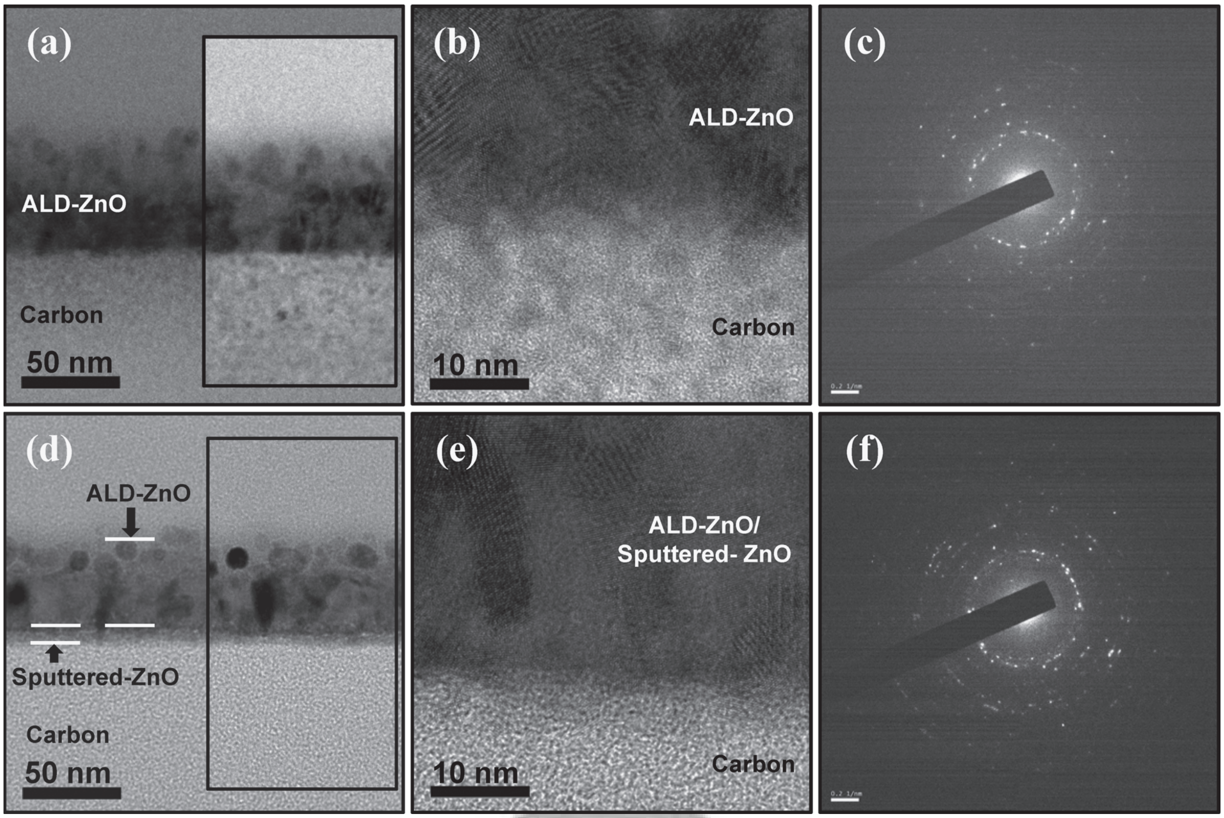

Fig. 2. TEM analysis results of ((a)–(c)) ALD-ZnO and ((d)–(f)) ALD-ZnO/sputtered-ZnO layers on the top region of the carbon post. (a), (b), (d), and (e) are the cross-sectional TEM images. (c) and (f) are the selected area electron diffraction patterns obtained from the ZnO layers. The insets of figure (a) and (d) are the TEM images obtained from the sidewall regions of the carbon posts.

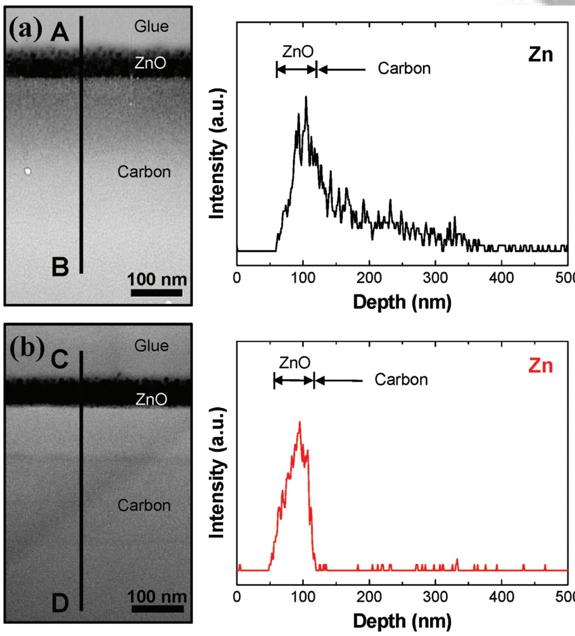

Fig. 3. TEM images and Zn concentration profiles measured from the EDS line scans obtained from (a) ALD-ZnO and (b) ALD-ZnO/sputtered-ZnO layers on the carbon post. A–B and C–D lines are the EDS scan lines and correspond to the *x*-axes of the right-side figures.

interfacial layer was incorporated between the ALD-ZnO film and carbon post electrode. As shown in Figures 2(d) and (e), the interfacial ZnO layer effectively prevented the formation of the carbon region with the alternating contrasts. Although the thickness of the sputter-deposited ZnO layer slightly decreased on the sidewall region of the carbon post (see the inset of Fig. 2(d)), the alternating contrast region was not also observed. For more detailed confirmation of the efficient blocking of the Zn diffusion, an additional EDS line scan of Zn atoms was performed on the ALD-ZnO/sputtered-ZnO/carbon post sample and its result is shown in Figure 3(b). No noticeable infiltration of the Zn atoms into the carbon was observed, which proved a role of the interfacial ZnO film as an efficient blocking layer of Zn diffusion during the subsequent ALD-ZnO process. When the ALD-ZnO film was formed on the sputter-deposited, interfacial ZnO layer, its thickness was similar to the thickness of the same film formed on the bare-Si wafer. According to the SADP obtained from the TEM sample (Fig. 2(f)), a hexagonal phase of ZnO layer was identified similar to the sample without the interfacial layer.

The surface morphologies of the ALD-ZnO layers with and without the interfacial ZnO diffusion barrier were carefully studied by taking SEM and AFM images on

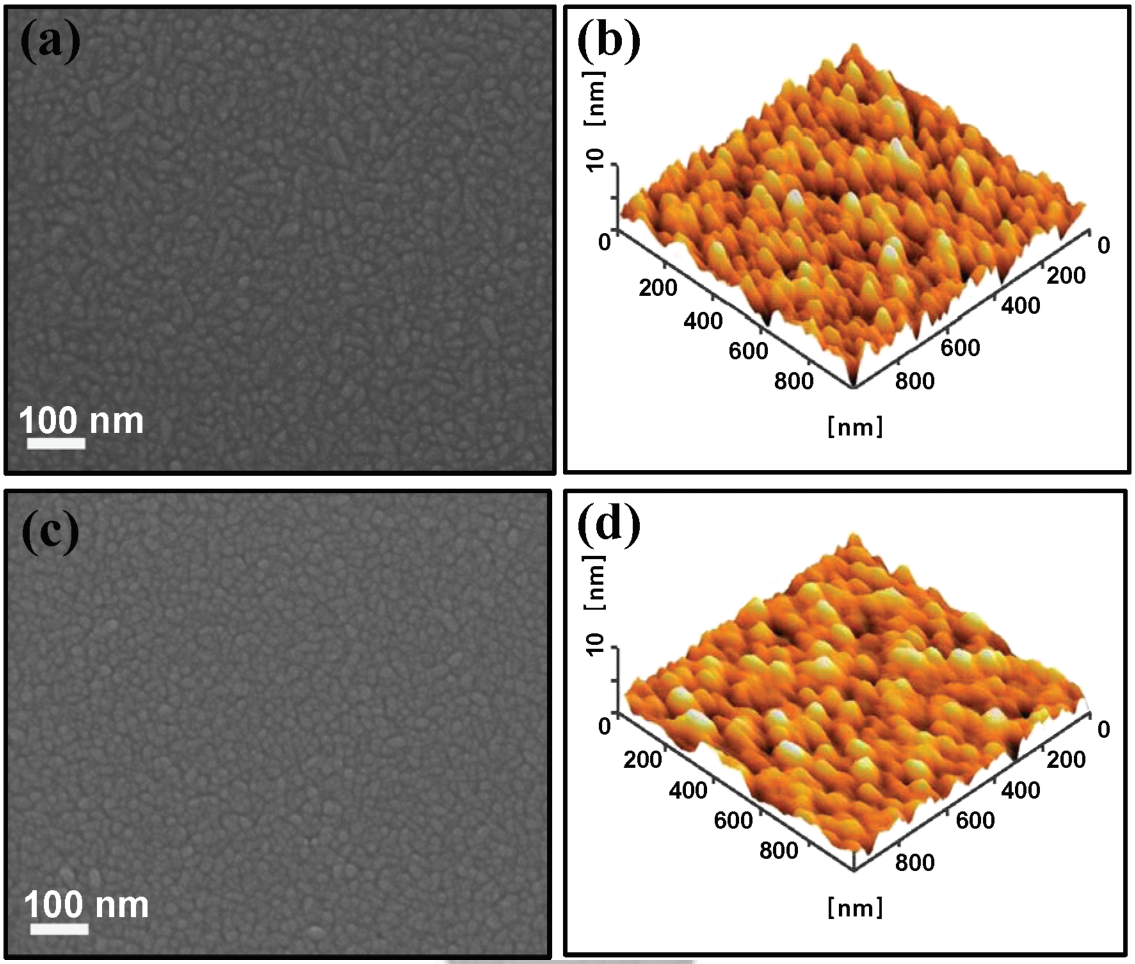

Fig. 4. Surface analysis results of the ALD-ZnO layers deposited on the carbon post: ((a) and (b)) without and (c) and (d)) with the sputtered-ZnO interfacial layer. ((a) and (c)) and ((b) and (d)) are the SEM and AFM images, respectively.

top of the carbon posts. As shown in Figures 4(a) and (c), nanometer-scale ZnO grains with similar surface morphologies were observed in both samples. According to the AFM measurement (Figs. 4(b) and (d)), no noticeable degradation of the surface roughness of the ALD-ZnO film was observed with the introduction the sputter-deposited ZnO interfacial layer; root-mean-square surface roughness of the ZnO films was ~0.7 nm and ~1 nm for the samples with and without the underlying ZnO interfacial layer, respectively. This implies that the extent of Zn diffusion can be effectively controlled with the sputter-deposited interfacial layer while the advantages of ALD are not compromised.

4. CONCLUSION

We investigated a surface modification method of conducting carbon post arrays prepared by two-step pyrolysis process after photolithography using an ALD-ZnO film. The ALD-ZnO process alone at 150 °C resulted in a conformal deposition of hexagonal ZnO film with nano-scale grains on the three-dimensional carbon post structure. However, a significant Zn diffusion into the underlying carbon layer was observed. In order to take advantage of a good quality ALD conformal oxide film while preventing diffusion, a 10 nm-thick ZnO film was sputter-deposited and used as an interfacial layer for the subsequent ALD process. This method efficiently prevented the Zn diffusion during the ALD process without compromising the microstructures and surface morphologies of the ALD-ZnO films. This study laid out a foundation for the ALD-based surface modification strategy applicable to the post-processing of the C-MEMS devices.

Acknowledgment: This work was supported by the World Class University (WCU) program through the National Research Foundation of Korea funded by the Ministry of Education, Science and Technology (Grant No. R32-2009-000-10124-0).

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Received: 20 November 2010. Accepted: 17 March 2011.