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Sputter deposition of ZnO nanorods/thin-film structures on Si

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Abstract

Using a recently developed sputter deposition technique, ZnO deposits were grown at the room temperature on silicon wafers with various kinds of copper surface layers. The copper layers were prepared using sputter deposition, thermal evaporation, or electroless plating technique. It was found that the surface copper prepared using both sputter deposition and thermal evaporation technique grew only ZnO thin films, while the surface copper prepared using sputter deposition technique grew ZnO nanorods/thin-film deposits. The relation between the copper characteristics and the growth of ZnO nanorods/thin-film deposits was investigated. The growth kinetics of the ZnO nanorods/thin film structure is also discussed.

Keywords: ZnO; Nanorods; Sputter deposition; Electroless copper

1. Introduction

Low-dimension materials such as quantum dots [1], nanowires [2], and quantum well [3] structures are being investigated for their superior properties and numerous applications [4–6]. Among them, one-dimensional semiconductor ZnO, representing one of the most important low-dimensional materials, finds its applications in many different fields [7]. For example, ZnO nanorods or nanowires are very useful in several nanostructure designs, including various semiconductor and electro-optical applications [8]. ZnO nanorods or nanowires are usually synthesized using vapor-phase oxidation of metallic Zn powders [9], vapor phase transport process via catalyzed epitaxial crystal growth [10], electrochemical deposition in anodic alumina membranes (AAM) [11], aqueous growth method [12], and hydrogen thermal method [13]. Despite of the diverse synthesis processes, a common mechanism used to explain the growth of ZnO nanorods or nanowires is the vapor–liquid–solid (VLS) mechanism.

Different from these processes and the VLS growth mechanism, we have reported in previous papers a new route for the growth of ZnO nanorods using a sputter deposition technique at the room temperature [14,15]. It was found that the existence of an electroless copper surface layer on the substrate is critical for the formation of ZnO nanorods. It also appears that the VLS mechanism fails to explain the growth process. In other words, the growth mechanism of ZnO nanorods obtained using the sputter deposition process is still unclear. Therefore, as a part of the effort to explore the growth mechanism, we have investigated the effect of various kinds of copper surface layers and ZnO deposition parameters on the formation of ZnO nanorods. The growth kinetics of the ZnO nanorods/thin-film structure is also discussed.

2. Experimental

The substrates used in this study were p-type Si wafers. An 80-nm-thick Ti layer was first deposited on the Si wafer using a sputter deposition method. A Cu layer was subsequently deposited on the Ti/Si substrate. The deposition of Ti was to prevent the interdiffusion between the Cu layer and the Si substrate. The Cu layer was deposited using three different methods, which were sputter deposition, thermal evaporation, and electroless plating methods. The sputter deposition of Cu was performed using a dc sputter

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deposition system. The thermal evaporation of Cu was performed under an Ar pressure of 1.334 Pa. The electroless plating of Cu was performed as follows. Solutions of $SnCl_2{\cdot}2H_2O$/HCl and ($PdCl_2$/HCl) were used, respectively, for the sensitization and activation of the substrate prior to the electroless plating. The electroless plating bath was composed of $CuSO_4{\cdot}H_2O$, potassium sodium tartrate, and formaldehyde. Two different basic bath compositions were used. In one of them, potassium sodium tartrate=2.5 g/100 ml, $CuSO_4{\cdot}H_2O$=0.5 ml/100 ml, and formaldehyde=1 g/100 ml (Type 1). In the other one, potassium sodium tartrate=3.0 g/100 ml, $CuSO_4{\cdot}H_2O$=1 ml/100 ml, and formaldehyde=2 g/100 ml (Type 2). Also, the pH value of the bath was varied by adding different amounts of NaOH into the bath. Different pH values ranging from 11 to 13 were obtained. The plating time was varied. During the plating, the bath was not heated. ZnO deposition was performed at the room temperature on the above substrates using an RF magnetron sputter deposition technique. The target used was ZnO (99.999%). The ZnO deposition time was fixed at 30 min. The deposition pressure was varied from 6.67 Pa to 0.667 Pa. The RF powers were 100 and 200 W and the electrode distance was 5 cm. The morphology, structure, and properties of the Cu layers and the ZnO deposits were characterized using scanning electron microscopy (SEM), X-ray diffractometry, energy dispersion of X-ray (EDX) analysis, and atomic force microscopy (AFM).

3. Results and discussion

3.1. Effect of the Cu layer on the growth of ZnO deposits

The characteristics of copper layers prepared using different methods were first compared. According to the XRD analysis, all the copper layers obtained exhibit the same crystalline structure. EDX analysis indicates that there is no residual from the plating bath left in the electroless copper. As the surfaces of all the copper layers were examined, it was found that they have different surface roughness. The surface of the sputter-deposited copper is the smoothest. The surface of the thermally evaporated copper is slightly rougher than that of the sputter-deposited copper. The surface of the electroless copper is significantly rougher than the thermally evaporated copper. The roughness of electroless Cu layer was found to increases with the pH value and the concentration of $CuSO_4{\cdot}H_2O$ in the plating bath, as shown in Fig. 1. It is also noted that the deposition rate of the electroless copper increases with the pH value and the concentration of $CuSO_4{\cdot}H_2O$. In other words, a thicker electroless copper layer has a rougher surface. As a result, two different kinds of ZnO deposits were found.

The ZnO deposits on either the sputter-deposited copper or the thermally evaporated copper are merely thin films. On the other hand, ZnO nanorods/thin-film

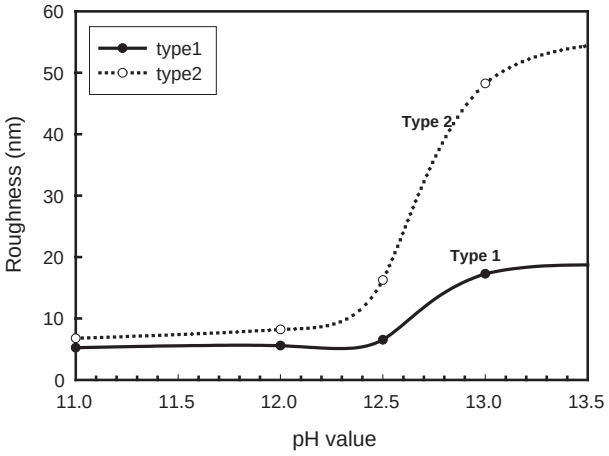

Fig. 1. Surface roughness of electroless copper as a function of pH value.

deposits were found on the substrates with electroless copper surface layers. However, not all the substrates with electroless copper surface layers grew ZnO nanorods/film deposits. In general, the surface roughness and the thickness of electroless copper appear to influence the formation ZnO nanorods. Fig. 2 compares ZnO deposits on surface copper layers with different roughness and thicknesses. The deposition pressure was 6.67 Pa. The ZnO deposit on an electroless copper layer having a low roughness (Ra=15 nm) and a small thickness (75 nm) is shown in Fig. 2A. Only a ZnO thin film is seen. As the roughness of electroless copper layer is increased by adjusting the pH value or plating time, formation of ZnO nanorods, as well as ZnO thin films, were observed. This is shown in Fig. 2B. The copper layer in Fig. 2B has a roughness of 45 nm and a thickness of 90 nm. When the thickness of the electroless copper layer was further increased, more ZnO nanorods were observed, as shown in Fig. 2C where the ZnO thin film is underneath the abundant nanorods and cannot be seen. The copper layer in Fig. 2C has a roughness of 47 nm and a thickness of 130 nm. It appears that the formation of ZnO nanorods requires an electroless copper surface layer with a minimum roughness of 40 nm and a minimum thickness of 90 nm, approximately. It also appears that the minimum roughness is a sufficient and necessary condition while a minimum thickness is only a necessary condition. Also, it seems that in ZnO nanorods/thin-film deposits, the area density of the ZnO nanorods increases with decreasing average grain size of ZnO thin film. This is shown in Fig. 3. The deposition pressure was 6.67 Pa. The average grain sizes of the ZnO thin films in Fig. 3A and B are, respectively, 80 nm and 150 nm. The former apparently has a higher area density of ZnO nanorods than the latter. However, it is really the average grain size of the electroless copper that affects the area density of ZnO nanorods. It has been found that an electroless copper with a larger average grain size results a ZnO thin film with larger average grain size [16].