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Ion beam sputter deposition of epitaxial Ag films on native oxide covered Si(1 0 0) substrates

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ABSTRACT

Epitaxial Ag films were grown on native oxide covered Si(1 0 0) substrates by an ion beam sputter deposition process at elevated deposition temperatures. At RT, films were observed to be non-epitaxial but with preferred (1 1 1) orientation. However, elevated substrate temperatures and under highly energetic sputter deposition process assist the growth of Ag films, that exhibit an epitaxial relationship with the underlying Si(1 0 0) substrates. With increasing deposition temperature an increase in the crystalline quality was observed with a narrowing mosaic distribution of crystallites and a decrease in the fraction of 1st order twins. The lowest epitaxial growth temperature was observed to be as low as 100 °C.

1. Introduction

Metal films on silicon substrates have been the focus of extensive study since past decades, as they offer unique applications in electronic, optical and magnetic devices [1–4], such as in Schottky barrier devices [5], optical filters [6], multilayered giant magnetoresistance materials [7] to name only a few. Particularly, Ag film on Si substrate presents an exemplary system that offers a metal/semiconductor interface required for the ideal metal contact and Schottky barrier application. Understanding the growth mechanism of an epitaxial film enables insight about the film properties and it aids to develop potential applications in various devices. Most of the previous investigations carried out regarding the epitaxial growth of Ag films are devoted towards molecular beam epitaxial (MBE) growth of Ag on oxide layer free Si substrates under ultra-high vacuum (UHV) conditions [8–10].

The growth of Ag on oxide free Si substrates in UHV condition presents an example of the Stranski-Krastanov (SK) growth mode, where growth of a wetting layer is followed by subsequent growth of three-dimensional islands. Therefore, an intensive amount of research has been devoted towards molecular beam epitaxial (MBE) growth of Ag on Si substrates. Additionally, with the MBE process it was shown that the deposited Ag films usually do not exhibit an epitaxial relationship with Si(1 0 0) substrates having a thin SiO_2 layer [11]. However, some studies concerning the growth of hetero-epitaxial layers on native oxide covered Si surfaces highlight a vital role of the native oxide [12–16]. Recently, Hur et al. reported the growth of radio-frequency magnetron sputter deposited Ag films on Si substrates covered with native oxide layer, that demonstrated a low epitaxial relationship with the underlying Si(1 0 0) substrate at a deposition temperature 200 °C, whilst a better epitaxial quality was observed at relatively elevated temperature at 550 °C [14,15]. The proposed mechanism suggests that the high energetic sputtered particles impinging the substrate surface at elevated deposition temperature enable the desorption of the native oxide from the Si surface, and thus allowing adatoms to reach the Si surface [2,14,15]. The presence of oxide layer on the substrate can alter the resulting growth dynamics as well as the properties of the grown film [12,13,16,17]. However, for impinging metal adatoms the oxide layer is locally desorbed allowing high energetic metal atoms to diffuse through such thin layer at high substrate temperature [2,14,15]. Therefore, the kinetic energy of impinging particles as well as the substrate temperature influence the growth of an epitaxial film on a native oxide covered Si substrate. In this case, the significant difference in the lattice constants of Ag and Si is compensated by a “3-to-4” matching condition [1,18–21], where the epitaxial growth of the Ag film on a Si(1 0 0) substrate is possible by cube-on-cube domain epitaxy. Moreover, in a recent study Chawla and Gall [22] described the growth of epitaxial Ag layers on MgO substrates and with a decrease in twinning of Ag layers with increasing growth temperature.

So far, the previous attempts to grow nano-crystalline epitaxial Ag films have been promising, however, the exact growth

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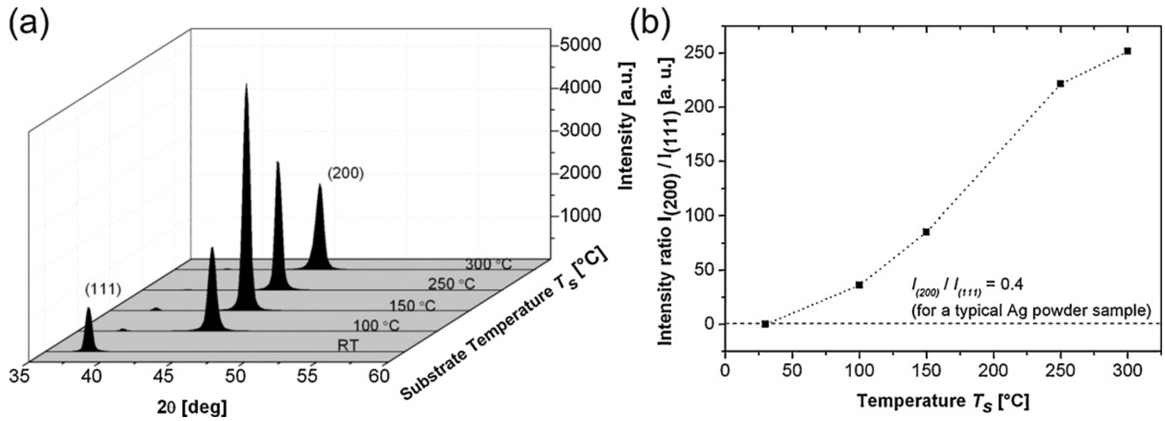

Fig. 1. (a) XRD $\theta/2\theta$ diffraction diagrams of Ag films deposited at various temperatures ranging from T_S = RT to 300 °C, (b) corresponding intensity ratio $I_{(2\,0\,0)}/I_{(1\,1\,1)}$ at different substrate temperatures.

mechanism of an epitaxial Ag film on such an amorphous native oxide covered Si(1 0 0) is not thoroughly understood. In this work, ion beam sputter deposition of Ag epitaxial films on native oxide covered Si(1 0 0) substrates is demonstrated. Detailed X-ray diffractometry (XRD), secondary ion mass spectrometry (SIMS), and scanning electron micrographic (SEM) analyses carried out on these films are presented here. The crystallographic texture of the films has been investigated for different growth temperatures ranging from room temperature (RT) to 300 °C. At RT, the films are observed to be polycrystalline with preferred (1 1 1) orientation, while at elevated deposition temperature they demonstrate a distinct epitaxial relationship with the underlying Si(1 0 0) substrate. The minimum epitaxial growth temperature was observed to be as low as 100 °C. For comparison, experiments on native oxide-free Si(1 0 0) substrates at elevated deposition temperatures were carried out, which exhibited a growth of non-epitaxial Ag films, signifying the key role of the native oxide layer.

2. Experiment

Ag films were grown on Si(1 0 0) substrates by the ion beam sputter deposition method. All the experiments were carried out in a high vacuum deposition chamber with a base pressure of 2×10^{-6} Pa. The experimental setup consisted of a polycrystalline Ag (purity 99.999%) target which was sputtered by an Ar^+-ion beam, extracted from a radio-frequency (13.56 MHz) ion source with a triple-grid ion extraction system (grid diameter 40 mm) as described elsewhere [23]. The working pressure during deposition was 8.5×10^{-3} Pa in the presence of the process gas Ar. The ion energy of 900 eV and Ar gas flow f_{Ar} = 4.4 sccm (standard cubic centimeters per minute) were kept constant for all experiments. The ion beam used to sputter the target surface reached the target at an angle of $\Phi_{Target} \approx 70°$ measured with respect to the target normal. The sputtered particles reached the substrate surface under near normal incidence conditions. The distances between source–target and target–substrate measured 0.15 m and 0.12 m, respectively. For this particular set of deposition conditions, the deposition rate was observed to be $r \approx 31.2$ nm/min. The substrate was rotated around the substrate normal at constant rotational speed ω = 0.2 rpm, with the aid of a computer-controlled step motor. Films with an approximate thickness of 500 nm thickness were grown. The deposition temperature was adjusted with a tantalum wire resistance heater and measured with a thermocouple. The films were grown at different temperatures ranging from room temperature (RT) to 300 °C. After the deposition, the samples were examined with scanning electron microscopy (SEM) at 2.5 kV acceleration voltage. The crystallographic structure and texture analysis of the samples was done using X-ray diffraction (XRD) (Cu-Kα_1 radiation) including texture goniometry using a four-circle goniometer. Both 2θ and χ values were taken from the reference values of the power diffraction file database entries for Si and Ag from the ICDD (International Centre for Diffraction Data) as following: for Si(1 1 1) φ scan: 2θ = 28.443° and χ = 54.74°; Ag(1 1 1) φ scan: 2θ = 28.116° and χ = 54.74°. Elemental depth profile measurements were performed using secondary ion mass spectrometry in a time-of-flight setup (TOF-SIMS) with 15 keV $^{69}Ga^+$ ions for the analysis and 2 keV Cs^+ ions for sputter depth profiling with a respective scan area of $75 \times 75\ \mu m^2$, centred in a sputter crater of $300 \times 300\ \mu m^2$ in size.

3. Results and discussion

Fig. 1(a) depicts XRD $\theta/2\theta$ diffraction diagrams of Ag films deposited at different substrate temperatures ranging from T_S = RT to 300 °C. The film deposited at RT was observed to be polycrystalline, but with a distinct preferred (1 1 1) orientation. Particularly, for a typical Ag powder sample, the ratio of intensity of (2 0 0) and (1 1 1) reflections is 0.4 [24]. Here it is observed to be ~0.002. With increasing deposition temperatures from T_S = RT to 100 °C, 150 °C, 250 °C and 300 °C, the intensity of the (2 0 0) reflection increased, while the intensity of the (1 1 1) reflection decreased. Even at a substrate temperature as low as T_S = 100 °C, the (2 0 0) reflection was observed to be stronger compared to the very low intense (1 1 1) reflection. The intensity ratio $I_{(2\,0\,0)}/I_{(1\,1\,1)}$ as a function of the substrate temperature from T_S = RT to 300 °C has been plotted in Fig. 1(b). Due to the dominant (1 1 1) reflection at RT, the intensity ratio was observed to be minimum. But for increasing substrate temperature from T_S = RT to 300 °C, the intensity ratio increased due to a highly intense (2 0 0) reflection. Thus, it can be concluded that the volumetric fraction of crystallites with (1 0 0) orientation increases with increasing substrate temperature.

As the intensity of (2 0 0) reflections was observed to increase with increasing substrate temperature, azimuthal scans of reflections corresponding to the Ag films and to the Si(1 0 0) substrates were accumulated. Fig. 2 illustrates such X-ray (1 1 1) φ-scans at a sample tilt angle χ = 54.74° of a Si(1 0 0) substrate (Fig. 2(a)) and of Ag films deposited at T_S = 100 and 300 °C (Fig. 2(b) and (c), respectively). The φ-scans of the Si(1 0 0) substrate demonstrates an extremely narrow FWHM (full width half maximum) for the observed equidistant four peaks, as it is expected for single crystalline material. The φ-scans of the corresponding Ag film deposited at T_S = 100 °C exhibits a single favourable in-plane orientation of (1 0 0) with four fold matching symmetry on the Si(1 0 0) substrate. It is evident that the Ag film exhibits an epitaxial relationship