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ScienceDirect
Nuclear Instruments and Methods in Physics Research B 266 (2008) 1480–1485
NIM B
Beam Interactions with Materials & Atoms
www.elsevier.com/locate/nimb

SIMS study of effect of Cr adhesion layer on the thermal stability of silver selenide thin films on Si

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Received 22 September 2007; received in revised form 20 November 2007
Available online 3 January 2008

Abstract

Effect of heat treatment on silver selenide films grown from diffusion-reaction of Ag and Se films on Cr-buffered Si substrates was investigated up to 400 °C. X-ray diffraction (XRD), Scanning electron microscopy (SEM), Secondary ion mass spectrometry (SIMS) and X-ray photoelectron spectroscopy (XPS) were used to characterize the films. XRD patterns of the films showed stress assisted change in preferential orientation of the films upon annealing: the films annealed at 200 °C exhibited a strong orientation along (200) plane, which changed to (013) after annealing at 300 and 400 °C. Dynamic SIMS measurements showed that Cr is confined to the interface and that there is no diffusion of Cr into silver selenide.

PACS: 61.05.cp; 82.80.Ms; 68.60.Dv

Keywords: Silver selenide; XRD; SIMS; XPS

1. Introduction

Silver selenide, which has long been known for its polymorphism and high ionic conductivity [1], is being studied with renewed interest after the recent reports of huge magnetoresistance in this material [2]. This observation assumes further significance as both Ag and Se are non-magnetic and stoichiometric silver selenide does not exhibit significant magneto-resistance. In addition, the linear dependence of magneto-resistance on magnetic field makes it a promising material for magnetic field sensors. In a previous paper [3], we have studied in detail the stability of silver selenide films grown on Si substrates, by the reaction of sequentially deposited Ag and Se thin films. However, our results showed that although the sequential deposition offered a simple way to grow thin films of silver selenide, the film morphology became unstable and agglomerated when annealed beyond 200 °C.

Adhesion of a thin film to a specific substrate is a key factor that determines dewetting and agglomeration of a uniform film during thermal processing. One of the effective methods to improve the adhesion of, for instance, a noble metal film to an oxide substrate is to insert a suitable layer between the metal film and the substrate [4]. Traditionally refractory metals such as Cr and Ti and their compounds have been employed for this purpose. The ability of these adhesion promoters to inhibit agglomeration has been attributed to their tendency to easily form sub-oxides, especially during the initial stages of growth. This enhances the adhesion as the oxide–oxide bond is shown to be much stronger than the noble metal-oxide bond. Additionally, the adhesion films do not easily diffuse into or undergo a chemical reaction with the metal films. The present work

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doi:10.1016/j.nimb.2007.11.029

aims at investigation of the effects of heat treatments on silver selenide thin films grown from diffusion-reaction of Ag/Se bilayers on Si substrates covered with a thin film of Cr. We present here for the first time clear evidence for the stress induced texture along (0 1 3) direction, in contrast to the thermodynamically favorable (0 0 2) direction.

2. Experimental details

The details of the growth of silver selenide thin films are given elsewhere [3]. Initially, a thin Cr film was deposited onto Si(1 0 0) wafers, which were treated with 10% HF followed by a high pure Ar (99.9%) glow discharge for about 20 min at a chamber pressure of ∼0.1 mbar. After the Cr deposition, the samples were taken out by breaking vacuum by introducing Ar and were loaded in another chamber for deposition of silver selenide thin films. The Cr/Si samples were, then exposed to an Ar glow discharge under similar conditions mentioned earlier for removal of any adsorbed water vapor. Silver selenide films were formed by first depositing Se film followed by the deposition of Ag film of suitable thickness. A quartz crystal thickness monitor was used to monitor the rate of deposition and the thickness of the films. The rate of deposition for the Ag (and Se) and Cr films was ∼10 and 0.1 $\text{Å}s^{-1}$ respectively. The thickness of the silver selenide film was about 160 nm and the Cr film thickness was in the range of 5–12 nm.

The as-deposited films were annealed at 100, 200, 300 and 400 °C as described elsewhere [3]. Phase identification was carried out with Cu K_α radiation using a PANalytical model X'Pert PRO XRD unit in the θ–2θ geometry. The sample morphology was probed using JEOL (model: JSM 840A) scanning electron microscope with an operating voltage of 15 kV. Dynamic SIMS measurements were performed using Cameca IMS-4F equipment with a 4 keV Cs^+ primary ion beam. The samples were kept at 2.25 kV, which resulted in a net 1.75 keV impact energy for the Cs^+ ion beam. The angle of incidence of the primary ions was 46.2°. The Cs^+ ion beam was rastered on the sample in an area in the range 150–250 μm^2 and the secondary ions were collected from a central 60 μm diameter optically gated area in order to reduce the crater edge effects. Positive cluster ions MCs^+ (M = Ag, Se, Cr, O or Si) were monitored to obtain the depth distribution of the corresponding element. These cluster ions are considered to be relatively free from matrix effects and are expected to give better quantitative results than the M^+ or M^- ions [5]. The depth profiling was continued until the Si signal reached a stable constant value, which was indicative of the fact that sputtered species originate from deep within the Si substrate. XPS measurements were carried out using an ESCA-2000 Multilab apparatus (VG Microtech) with a non-monochromatic Mg K_α excitation source and a hemispherical analyzer. The binding energies of the core levels were corrected with reference to C 1s line at 284.6 eV.

3. Results and discussion

3.1. XRD studies

Typical XRD patterns of the as-deposited films and those annealed at 100, 200 300 and 400 °C are presented in Fig. 1. In the as-deposited film (Fig. 1(a)), the sharp peaks indicating polycrystalline nature of the sample are indexed according to the orthorhombic phase of Ag_2Se (JCPDS file: 24-1041). The XRD pattern of the film annealed at 100 °C (Fig. 1(b)) is similar to that of the as-deposited film, however, with a slight variance in the peak intensities. For example, the intensity of the (0 3 1) peak has increased while that of the (1 0 2) and (1 2 1) peaks is reduced in comparison with those of the as-deposited film. Annealing at 200 °C has brought about a huge change in the XRD pattern of the films (Fig. 1(c)). Fig. 1(c) shows large increase in the intensity of (0 0 2) peak (and that of the (0 0 4) peak, as expected). Besides these two peaks, there are traces of only three peaks, namely (1 1 2), (0 1 3) and (0 1 4) seen in the pattern. The other peaks including the (0 3 1) peak, the highest intensity peak in the as-deposited and the 100 °C-annealed films are missing completely. The growth of the (0 0 2) and (0 0 4) peaks at the expense of the other peaks clearly indicates a strongly preferred (0 0 2) orientation of the films.

When the annealing temperature is increased, a change of preferred orientation of the films is noticed. At an annealing temperature of 300 °C (Fig. 1(d)), decrease in

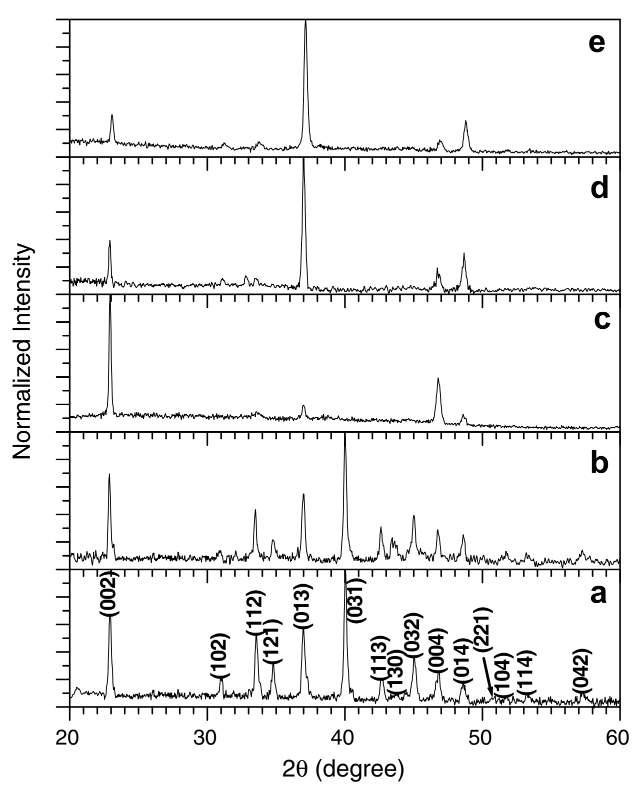

Fig. 1. Typical XRD patterns of silver selenide thin films grown on ∼5 nm thick Cr film-covered Si substrates: (a) as-deposited film and those annealed at (b) 100, (c) 200, (d) 300 and (e) 400 °C.