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Solid-state dewetting of continuous thin platinum coatings

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ABSTRACT

Thermal stability of coatings is of crucial importance for reliability of electronic devices operating at high temperature. Thus, we investigated the Cr–Pt system where a thin platinum coating of 0.1 μm was deposited on chromium substrate and annealed at 1000 °C for 8 h. The scanning electron microscope (SEM) showed that a continuous and uniformly deposited Pt coating experienced the formation of "islands" after annealing. The grain-boundary grooving, dewetting and agglomeration were the main mechanisms of degradation of thermally annealed coatings. Results by μ-PIXE (particle-induced X-ray emission) and transmission electron microscope (TEM) showed the presence of Cr_3Pt phase in "islands" and the coating thickness was approximately 0.5 μm. The surrounding regions were left uncovered due to coating agglomeration at the expense of initially deposited coating.

1. Introduction

The thermal stability of metallic polycrystalline films is of significant importance for their applications in the microelectronic industry. The coatings can break into islands or droplets when sufficient activation energy is supplied. This phenomenon is known as dewetting or agglomeration and it can be responsible for the breaking of electrical interconnections. Coatings are thermodynamically unstable due to an increase in the structural defects present that raise the surface free energy and when thermally annealed they can undergo processes of dewetting and agglomeration to minimise this energy increase [1]. Agglomeration of polycrystalline films is a mass transport process by which the substrate material initially covered by a continuous coating undergoes dewetting, leaving the substrate partially uncovered. The coatings become rough when heated as a result of dewetting which induces the formation of voids in the coating [1]. The coating can agglomerate if the surface energy exceeds the sum of the interfacial energy and surface energy of the substrate resulting in the dewetting process at elevated temperatures. Saxena et al. investigated the atomistic mechanisms of dewetting in thin films [2]. Their research shows that for thicker films (>20 nm) grain boundary grooving is the rate limiting step that controls agglomeration or complete island formation. This is owing to grain boundary grooving having the highest activation energy which in turn limits the formation of voids. As a result of this, the coating islands were formed. GB-grooving is driven by a tendency to reduce the system grain boundary energy [3]. The processes of dewetting and agglomeration have been observed with platinum thin films for production of nanostructures for microelectronic devices [4,5].

The Cr–Pt coated system was used in this study as a model system to investigate the stability at high temperature. The changes in coating morphology and thickness as well as the phase transformation were characterised using different techniques. However, the μ-PIXE and TEM were seen as the most powerful techniques in this regard.

2. Materials and characterisation techniques

Chromium pieces of 99.98% purity used as substrate material were polished and cleaned prior to deposition of 0.1 μm thick coating of pure platinum (99.99%). The coating was deposited using electron-beam deposition technique under high vacuum conditions (1×10^{-5} Pa) at a rate of 2.4 Å/s and a current of 150 mA. The coating thickness was determined by monitoring using a quartz crystal sensor. After deposition, the coated samples were thermally annealed at 1000 °C for 8 h in vacuum at rate of 10 °C/min during heating and cooling stages. In order to understand the mechanism of solid-state dewetting of Cr–Pt coated system, we used several characterisation techniques. The coating morphology was investigated by scanning electron microscope (NOVA NANOSEM 230) and imaging was performed at 20 kV in both, the secondary electron (SE) and backscattered electron modes (BSE). The phase transformation was studied using X-ray diffraction. The measurements were carried out using a BRUKER

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D8-ADVANCE diffractometer coupled with a Vantec-1 position sensitive detector. Data were collected between 30° and 85° in 2θ at a step size of 0.03°. In order to get better statistics, the measurements were performed while the sample was rotating. The changes in coating thickness and composition caused by annealing were evaluated using Rutherford backscattering spectrometry (RBS) with a 3.0 MeV proton beam of 2 mm diameter and at the current of 32 nA. The RBS data were evaluated by RUMP software package [6]. The μ-PIXE technique was used to determine two-dimensional distribution of Pt and Cr elements. A proton beam of 3.0 MeV energy and current of 100 pA was focused to a $3 \times 3\ \mu m^2$ spot size and total area scanned was approximately $73 \times 73\ \mu m^2$. Experimental data were collected in list mode (event-by event) using XSYS data acquisition system and then processed using the GeoPIXE II software package. The spatial distribution of both elements was analysed and displayed as elemental maps using contour plots by IDL [7]. The elemental concentration was also investigated by transmission electron microscope (TEM). The samples were prepared by milling using focused ion-beam (FEI Helios NANOLAB 650 FIB-SEM). In order to maintain the coating integrity during ion milling, the samples were coated with a carbon layer deposited using ion beam assisted chemical vapour deposition (as a part of the FIB-SEM). After deposition of the C layer, the Ga^+ ion beam operated at 30 kV, was used to mill the samples in cross section. An Omniprobe lift-out needle was used to transfer the milled section to a Cu grid, where final polishing using the Ga^+ ion beam was completed at 500 eV to a TEM sample thickness of 50 nm. A JEOL 2100F TEM was operated at an accelerating voltage of 200 kV and imaging was performed in the STEM mode. The composition was determined using energy dispersive spectroscopy (EDS), as part of the STEM mode in the TEM. The measurements were taken in line scans across the coating and substrate regions.

3. Results and discussion

The morphology of as-deposited Pt coating and its changes due to exposure to elevated temperature are shown in Fig. 1. A smooth surface was observed in as-deposited coating (a) while the grain-boundary (GB) grooving, dewetting and agglomeration appeared to be the modes of coating degradation that occurred during thermal annealing (b and c). Considering the agglomeration, the SEM images show formation of islands. The island morphology refers to the coating aggregating towards the middle of the Cr grain (outlined by GB-grooves) and residing on its surface. A high magnification image (c) shows that there is separation in some areas within individual islands, it refers to sub-island-type morphology.

The phase analysis results of the 0.1 μm Pt coating in as-deposited condition and after annealing at 1000 °C for 8 h are shown in Fig. 2. The X-ray diffraction patterns show the Cr and

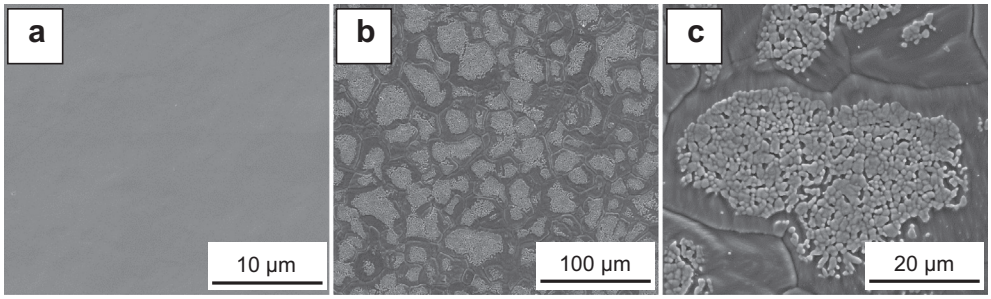

Fig. 1. SEM images show the smooth morphology of as-deposited condition (a), the grain-boundary grooving, agglomeration and formation of islands (b and c) were observed after thermal annealing.

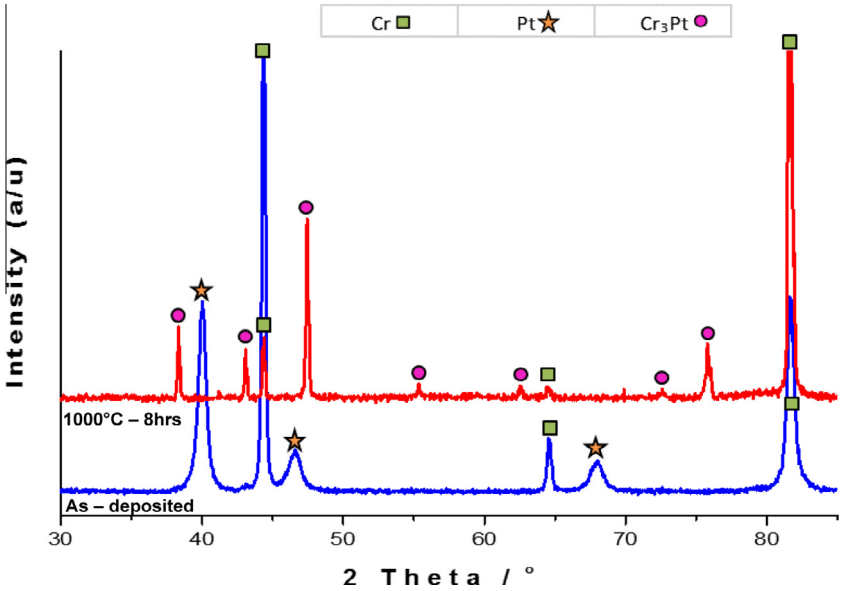

Fig. 2. X-ray diffraction patterns of deposited and annealed Cr–Pt coated system.