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Morphological stability of Pt coatings deposited on Cr substrates

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ABSTRACT

The morphological stability of coatings is an important factor for the reliability of microelectronic devices operating at elevated temperature. The focus of this work was to characterise and explain the coating degradation mechanisms of Pt–Cr coatings and thereby to find ways of extending their operating temperature range. Platinum coatings on chromium are shown to be morphologically stable up to 800 °C; at higher temperatures degradation is observed. Scanning electron microscopy of coated specimens with a systematic variation in both coating thickness and annealing temperature shows that significant grain-boundary grooving and agglomeration can occur. This has important implications for the reliability of microelectronic devices operating at elevated temperatures.

1. Introduction

Thin coatings are widely studied for applications in microelectronics and semiconductor devices [1–4]. The coating morphology is of importance because the structure of the coating can be compromised at high temperature: thermal annealing at high temperature can result in structural defects, so that the coating formed is non-uniform, discontinuous and degraded in morphology [5–7].

The formation of polycrystalline coatings by vapour deposition occurs by typical nucleation and growth processes which result in a uniform and equiaxed grain structure. During the deposition process, vaporised atoms are directed onto the substrate surface, and clusters of these atoms collect uniformly on the substrate surface and incorporate more atoms, until a subcritical level is reached. Small islands of these clusters nucleate so that island density increases across the surface. As the deposition process is continued the islands merge by coalescence, eventually resulting in a continuous coating across the substrate surface. The mechanisms of growth of a coating can occur in three different modes [8]: (1) island growth (Volmer–Weber) mode in which atoms in the deposit are more strongly bound to each other than to the substrate, resulting in clusters which nucleate on the substrate and form islands; (2) layer growth mode, in which atoms are more strongly bound to the substrate than to each other resulting in the formation of layered sheets of deposit; (3) an intermediate of these two growth modes, the Stranski–Krastanov growth mode, which can occur where one or more monolayers of the deposit are formed on the substrate surface and thereafter islands nucleate as the corresponding layer growth becomes unfavourable. The establishment of the coating introduces new surfaces and interfaces as well as many structural defects, which provides an increase in the surface energy of the system [8]. The dominant growth mode depends on the surface energy ratio (W) given by Eq. (1).

$$W = \frac{\gamma_s - \gamma_f}{\gamma_s} \tag{1}$$

where (γ_s) and (γ_f) are the interfacial tensions of the substrate and coating respectively.

The nucleation and growth modes during coating formation influence the coating morphology after thermal annealing; they are accordingly of critical importance from a practical point of view. The success of coating technology depends on the ability to maintain coating integrity during processing and service. Continuity of coatings is very often difficult to preserve due to their thermodynamic instability at elevated temperature. Several common failure modes, such as grain boundary (GB) grooving, agglomeration and formation of islands, have been reported to occur in polycrystalline metallic coatings [7,9,10].

GB grooving occurs when, in order to balance surface tension with GB tension, grooves are formed where GBs intersect the coating–substrate interface. GB grooving, also known as thermal grooving, is a well-known cause of agglomeration of thin films and coatings and it is driven by the tendency to reduce GB energy and thus serves as an important mechanism for morphological breakdown of thin coatings at elevated temperature [6]. The theory of Mullins [9] explains GB grooving

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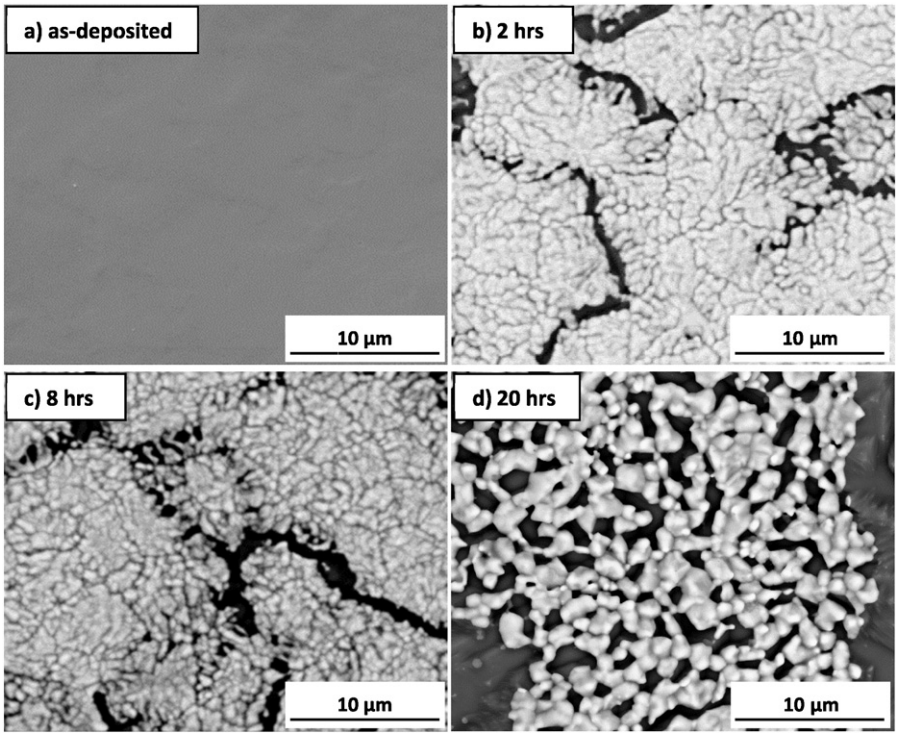

Fig. 1. SEM images showing the changes in the surface coating morphology of samples with 0.1 µm Pt deposited on Cr substrate (a) and thermal annealed at 1000 °C for varying times (b–d).

in terms of surface diffusion, volume diffusion and evaporation condensation with the gradient of surface curvature being the driving force.

Solid-state dewetting or agglomeration of polycrystalline coatings as a mass transport process uncovers the surface of the substrate in order to reduce the total free energy of the system. Agglomeration transforms the initially continuous coating into an island-like structure or an ensemble of isolated particles [7]. It is a common problem in many technological applications in which the coating integrity and continuity are of importance [11,12]. However, this phenomenon can be beneficial in some instances: individual "thermal-sub-islands" can serve as seeds for growing a variety of nano-structures [13,14].

The Cr–Pt coated system investigated in this study was used as a model system to study the stability of Pt connectors in microelectronic devices. The stability of Pt coatings was investigated as a function of thermal annealing temperature and time. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) were used to characterise the changes in coating morphology at structures caused by elevated temperature. The main focus of this study, however, was to find ways of extending the temperature range of this coated system without compromising its integrity. Therefore thicker Pt coatings were also investigated to determine if the morphological stability of the coatings is achieved at higher temperatures.

2. Materials and methods

Chromium (Cr) of 99.98% purity was used as substrate material; chromium substrate specimens were polished and cleaned prior to deposition of platinum (99.99% purity). Platinum coatings with thickness of 0.1 µm, 0.2 µm and 0.3 µm were deposited using electron-beam deposition. Deposition was performed at a rate of 2.4 Å/s and a current of 150 mA under high vacuum conditions (1×10^{-5} Pa). After deposition, samples were thermally annealed at temperatures from 700 °C to 1000 °C with slow furnace cooling; both heating and cooling rates were 10 °C/min. Complementary techniques were used for coating characterisation. The morphology of deposited coatings and the changes caused by thermal annealing were investigated by scanning electron microscope (SEM). A NOVA NANOSEM 230 was used at 20 kV to image the surface morphology in both the secondary electron (SE) and backscattered electron (BSE) modes. The effects of deposition and thermal annealing processes on phase formation were studied using X-ray diffraction (XRD). The XRD measurements were carried out using a BRUKER D8-ADVANCE diffractometer coupled with a Vantec-1 position sensitive detector. Data were collected between 20° and 90° in 2θ at a step size of 0.03°. In order to acquire better statistics, the measurements were performed while the sample was rotating.

3. Results and discussion

3.1. Surface morphology

We first investigated the integrity of the 0.1 µm Pt coatings annealed at high temperature (1000 °C) for annealing times up to 20 h. In the as-deposited coating, a smooth surface with no distinct features was observed as shown in Fig. 1(a). Annealing at 1000 °C resulted in coating degradation by grain-boundary (GB) grooving and agglomeration, Fig. 1(b–d). The morphological evolution with annealing time as shown in Fig. 1 revealed a change from compact "thermal island"-like structures at the shorter annealing times to that of a less dense structure after longer annealing times. The "thermal island" morphology refers to the coating aggregating towards the middle of the Cr grain (outlined by GB-grooves) and residing on its surface. With an increase in thermal annealing time to 20 h, shown in Fig. 1(d), clear separation within individual islands and the formation of "thermal sub-islands" were observed.

The observed thermal instability of coatings at 1000 °C can be explained by a number of factors. The total free energy of a coated system increases due to the formation of interfaces, both during deposition (predominantly the substrate/coating interface) and during any subsequent phase transformations (the new phase interface). To lower the total (Gibbs) free energy the coated system responds by changes in the coating morphology which lower the total free energy, particularly when the coated system is exposed to thermal annealing. This is because at high temperatures new phases form which create new