Acta Materialia 140 (2017) 149–156

Contents lists available at ScienceDirect

Acta Materialia

journal homepage: www.elsevier.com/locate/actamat

Full length article

In-situ study of the dewetting behavior of Au/Ni bilayer films supported by a SiO_2/Si substrate

Xi Cen, Andrew M. Thron, Klaus van Benthem*

Department of Materials Science and Engineering, University of California, Davis, CA 95616, USA

ARTICLE INFO

Article history:
Received 12 June 2017
Received in revised form
10 August 2017
Accepted 13 August 2017
Available online 14 August 2017

Keywords:
Bilayer
Dewetting
In-situ
STEM
Agglomeration

ABSTRACT

Solid state dewetting of Au/Ni bilayer films was investigated by in-situ cross-sectional TEM heating with energy-dispersive X-ray spectroscopy. The early stage of dewetting process revealed both grain boundary grooving at the surface of the Ni layer and void nucleation along the Au/Ni interface between Au grains. During annealing, inter-diffusion occurred and enhanced solubility was found between Au and Ni. Au diffused predominantly through Ni grain boundaries and decorated the Ni/substrate interface. The energetically preferred adsorption of Au at the Ni/SiO_2 interface and at Ni grain boundaries, coupled with some alloying in the volume of the metal films delays the break-up of the bilayer film compared to pure Au or Ni films. The experimental observations confirm that dewetting kinetics of metal bilayer films are strongly affected by both partial alloying of the metals as well as the metal/metal interface.

1. Introduction

Solid state dewetting [1,2] refers to the break-up of kinetically constrained thin solid films at elevated temperatures. The driving force for this process, which is often referred to as ‘agglomeration’, is the minimization of the total free energy of film and substrate free surface and film-substrate interface, including consideration of potential inter-diffusion and solid-state reactions [3]. Dewetting adversely affects the thermal stability of thin film micro- or nanoelectronic devices [4]. It can, however, also be useful for generating arrays of nanoparticles and nanowires [5–7], hence impacting manufacturing of transistors [8], catalysis [9], or energy storage [10]. Mechanisms for solid state dewetting of single layer films have been studied extensively. An imbalance of surface and grain boundary energies causes the diffusion away from the grain boundary, hence forming a grain boundary groove. Once grooving reaches the film/substrate interface, a hole is formed between two separate parts of the film [11]. Alternatively, high defect energies at grain boundaries along the film/substrate interface can cause void nucleation and growth [12]. Continuous growth towards the free surface of the film subsequently leads to the formation of holes. Holes formed in the film will grow by capillarity driven diffusion, which ultimately leads to the formation of individual islands on the substrate surface, i.e., film agglomeration.

Dewetting transitions of bilayer films are expected to be strongly affected by the interaction between the different components. For instance, alloying between two elements has been shown to enhance thermal stability of bilayer or alloyed films upon annealing [13–15]. The underlying kinetics that cause any delay of film agglomeration were, however, not experimentally confirmed. In contrast, the addition of immiscible Ag into Ni films was observed to initiate by fractal-like growth of holes rather than expected capillarity driven hole nucleation by grain boundary grooving [16]. It was suggested that the creation of local tensile stress caused by the segregation of Ag enhances the agglomeration of vacancies and pore formation at specific sites, which causes hole formation. However, no experiments were carried out to verify the correlation between the segregation of Ag and increases in local tensile stress. Dewetting of Ni-Cr alloyed [17] films under different annealing conditions revealed a variety of dewetting behaviors resulting from surface oxidation and film-substrate interaction due to different oxygen affinities of the two metals [17]. Studies of Ag/Co bilayer films [18] revealed that film deposition sequence and solubility between two elements affect the microstructural transitions during a pulsed laser induced dewetting process.

For this study the Au/Ni bilayer system was chosen because of the presence of a miscibility gap at room temperature and increasing solubility of one metal in the other for temperatures up

---

* Corresponding author.
E-mail address: Benthem@ucdavis.edu (K. van Benthem).

http://dx.doi.org/10.1016/j.actamat.2017.08.027
1359-6454/

to 816°C [19]. Early dewetting studies of Au/Ni bilayer films in argon ambient showed that the temperature-dependent solubility affects the kinetics of hole formation [20] and morphology of islands on the substrate surface [21]. Supersaturated Au/Ni particles form when a Au/Ni bilayer film is annealed at temperatures above the miscibility gap and subsequently quenched [22]. High elastic energy at the interface between Ni- and Au-rich phases favors the formation of ⟨100⟩ facets on the surface of Ni-rich precipitates in Au-Ni bimetallic islands [23]. Unlike commonly assumed homogenous dewetting in single constituent polycrystalline films, Au/Ni bilayer films exhibited different behaviors when isothermally annealed in vacuum. The Ni layer was observed to homogeneously agglomerate, while long-range edge retraction occurred for the Au layer. This behavior was attributed to the unstable Au/Ni interface and the difference in the self-diffusion coefficient between the two metals [24]. Ex-situ cross-sectional transmission electron microscopy (TEM) studies were employed to investigate the early stage of film agglomeration [25,26]. After annealing for 1 h at 675 °C, the Ni/SiO_2 interface was replaced by the energetically more favorable Au/SiO_2 interface. Void nucleation was found to be the dominant mechanism for the nucleation of holes during the early stages of film agglomeration. Previous ex-situ TEM characterization post annealing has shown significant changes in film morphology and the arrangement of Au and Ni. Formation of Au/SiO_2 interface without film agglomeration was found to delay the dewetting process. However, the kinetic pathways for this chemical rearrangement remained unclear. Grain boundary diffusion of Au through the underlying Ni film was proposed, but needs to be verified through in-situ annealing experiment reported in this study. The dewetting kinetics of Au/Ni bilayer films were investigated by in-situ TEM heating experiments coupled with the analysis of local chemical composition. The experimental observation suggests that the bilayer dewetting process is strongly affected by alloying of Au and Ni as well as the metal/metal interface.

2. Experimental details

Nickel and gold films were consecutively deposited onto Si

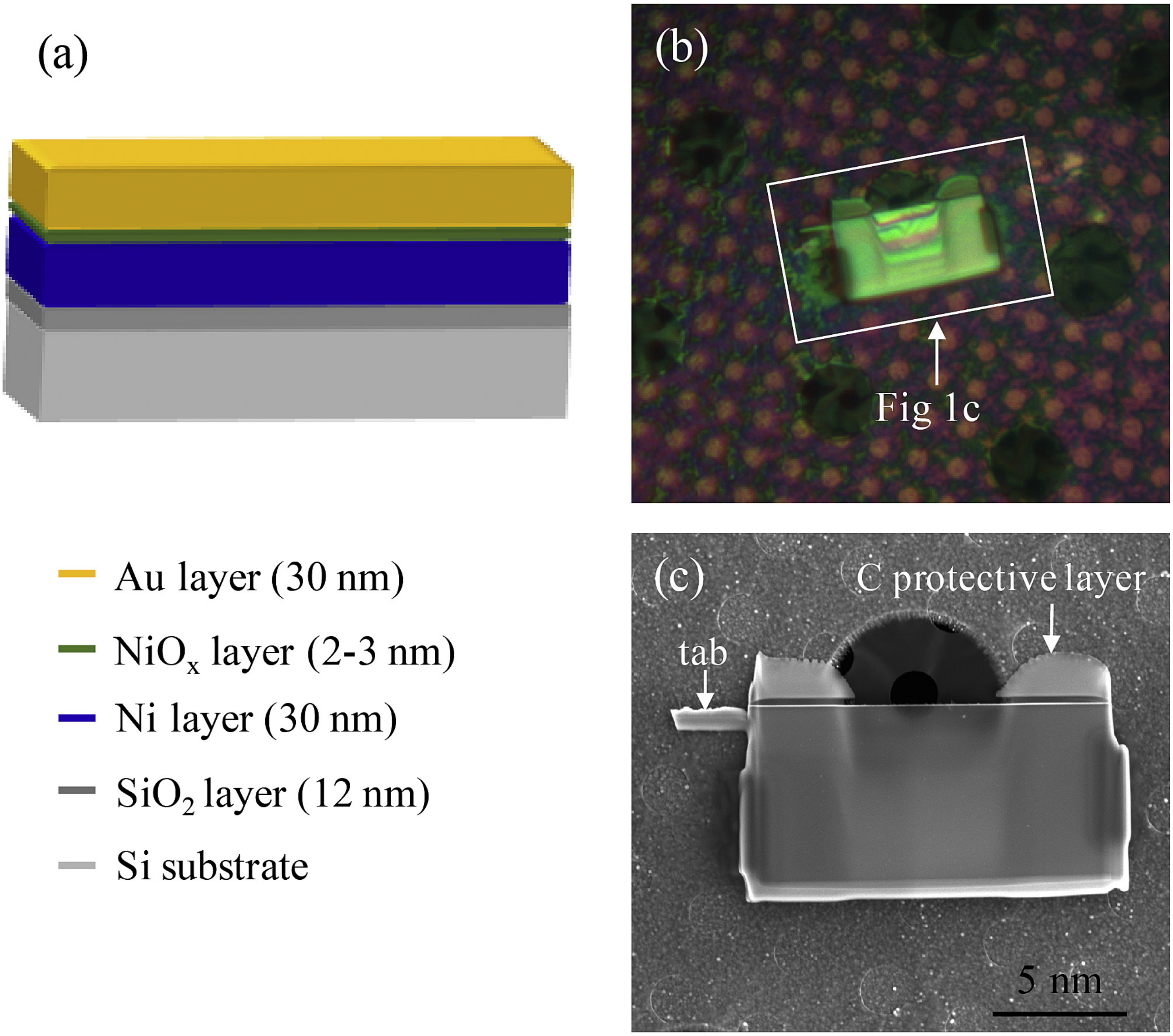

Fig. 1. (a) Sketch view of the as-deposited metal bilayer film. Ni and Au were sequentially sputter deposited on top of SiO_2/Si substrates. NiO_x formed as a native oxide after Ni deposition. (b) Plan-view light microscopy image of an electron transparent TEM lamella placed onto the heating membrane of an in-situ TEM sample holder. (c) is a magnified SEM micrograph of the area indicated in (b).