Cross-sectional characterization of the dewetting of a Au/Ni Bilayer Film

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Abstract

The solid state dewetting of Au/Ni bilayer films was investigated by cross-sectional transmission electron microscopy techniques, including energy-dispersive X-ray spectroscopy, electron energy-loss spectroscopy and precession electron diffraction. After annealing under high vacuum conditions the early stage of film agglomeration revealed significant changes in film morphology and chemical distribution. Both Au and Ni showed texturing. Despite the initial deposition sequence of the as-deposited Au/Ni/SiO₂/Si interface structure, the majority of the metal/SiO₂ interface was Au/SiO₂ after annealing at 675°C for 1 hour. Void nucleation was predominantly observed at Au/Ni/SiO₂ triple junctions, rather than grain boundary grooving at free surface of the metal film. Detailed cross-sectional characterization reveals that the Au/Ni interface in addition to small amounts of metal alloying strongly affects film break-up and agglomeration kinetics. The formation of Au/SiO₂ interface sections is found to be energetically preferred over Ni/SiO₂ due to compressive stress in the as-deposited Ni layer. Void nucleation is observed at the film/substrate interface, while the formation of voids at Ni/Au phase boundaries inside the metal film is caused by the Kirkendall effect.

Keywords: Gold/nickel bilayer film; Dewetting; Void formation

1. Introduction

Solid state dewetting is a result of an imbalance between interface and surface free energies for a thin film on a solid substrate [1, 2]. Thin film agglomeration can be a serious inter-circuit breaking issue in microsystem fabrication [3], while the mechanisms can also be used for preparing self-assembled arrays of catalyst for the growth of nanotubes and nanowires [4-6]. Hence, a comprehensive understanding of the mechanisms of solid-state dewetting is important for controlling processing steps in the fabrication of microelectronics and arrays of self-assembled catalyst sites. Agglomeration of polycrystalline films can be initiated by grain boundary grooving where the grain boundary intersects the free surface of the film, or by the formation of voids at the film/substrate interface [7, 8]. Once a hole in the film has formed, it will grow subsequently by continuous diffusion exposing the free surface of the underlying substrates [9]. Wetting-dewetting transitions have been extensively studied in single component films, but only few studies are reported for multi-component films [10-18].

Alloying and interdiffusion have been shown to affect the wetting and dewetting transitions in multi-component and bilayered films. Alloying of Au films with small amounts of Pt was observed to delay the onset of dewetting, while the underlying kinetics that caused the delay were not experimentally confirmed [10]. The addition of Ag into Ni films was shown to induce a fractal-like growth mode of voids rather than the expected capillarity driven hole nucleation and growth initiated by grain boundary grooving [11]. Dewetting of Ni-Cr alloyed films showed that different annealing conditions resulted in a variety of dewetting behaviors due to surface oxidation and film-substrate interaction, which were affected by different oxygen affinity of the two metals [12]. Single crystal

Au/Fe and Fe/Pd bilayer films showed enhanced thermal stability upon annealing due to alloying effects [13, 14].

The Au/Ni bilayer model system used in this work, shows a homogeneous solid solution for temperatures above 816°C, and a varying miscibility below 816°C [15]. Early studies on Au/Ni bilayer dewetting in Ar ambient revealed that the morphology of dewetted islands varies with annealing temperatures due to variations in the solubility limits [16-18]. Alloying starts to delay the hole formation above 700°C due to the formation of an intermediate phase [17]. Supersaturated, submicron-size Au-Ni islands can form when a Ni/Au bilayer film is annealed at temperatures above the miscibility gap, and subsequently quenched [18]. Phase separation from supersaturated Au/Ni particles was investigated by cross-sectional scanning electron microscopy (SEM) after additional annealing at 650°C [19]. It was found that at equilibrium, the Ni-rich phases formed $\langle 100 \rangle$ facets, rather than the $\langle 111 \rangle$ facets. A preference toward the $\langle 100 \rangle$ facets was attributed to a minimization of elastic energy at the interface between the Ni and Au rich phases. The studies reviewed above were mostly focused on how the amount of alloying affects the agglomeration behavior of Ni/Au bilayer films. Interface configurations during the early stages of bilayer film agglomeration are not reported in the literature, but are critical for a detailed understanding of the break-up behavior of multi-component thin films. Void nucleation and thermal grain boundary grooving were previously discovered by cross-sectional SEM imaging [17]. More detailed transmission electron microscopy (TEM) characterization is, however, required to interrogate the changes in structural morphologies and chemical distributions.

In this study we report changes in chemistry and microstructure of Au/Ni bilayer film during isothermal annealing, and the effects these changes have on the agglomeration of the bilayer film. Changes in the morphology and microstructure were observed by cross-sectional transmission electron microscopy (TEM) techniques, including scanning transmission electron microscopy (STEM), precession electron diffraction (PED), electron energy-loss spectroscopy (EELS) and energy-dispersive X-ray spectroscopy (EDXS). The experimental results reveal dominant void nucleation at Au/Ni interfaces within the film and at the bilayer/substrate interface, strong texturing of both metals as a function of diffusivity, and rearrangement of phase separated Au and Ni grains strongly affected by the compressive stress state in the as-deposited metal films and different diffusivities between two elements.

2. Experimental Details

Nickel and gold film were sequentially deposited onto Si substrates each with a nominal thickness of 30 nm. Prior to metal film deposition a 12 nm SiO₂ thick layer was thermally grown on the (100) surface of silicon substrates to avoid silicide formation [20]. Ni films were deposited at room temperature by DC magnetron sputtering at a power of 100 W, a base pressure of 1.7×10^{-8} torr, and an Ar atmosphere of 2 mtorr. The corresponding sputter rate was $1.4 \text{ \AA s}^{-1}$. Au films were subsequently deposited on top of Ni at room temperature, using a Denton vacuum desk II cold sputtering unit. Au sputtering was performed at a base pressure of 20 mtorr, and an Ar pressure of 75 mtorr. The sputtering current was set at 23 mA resulting in sputtering rates around $2.5 \text{ \AA s}^{-1}$. Prior to deposition the SiO₂/Si substrates were cleaned by sonication in methanol and deionized water immediately before insertion into the deposition chamber.

The as grown samples were annealed in a three-zone tube furnace (Lindberg) at a base pressure of 6×10^{-6} torr at 675°C for 1 hour. To avoid contamination the samples were placed in an alumina boat during annealing. Fast heating and cooling were achieved by pushing and withdrawing the quartz tube containing the samples into and out of the hot zone of the furnace [21].

Cross-sectional TEM specimens were prepared by standard FIB lift-out techniques [22,23] using a FEI Scios dual-beam instrument. Film morphology and microstructures were characterized using a JEOL JEM-2500SE transmission electron microscope. STEM annular dark field (ADF) imaging was carried out with a FEI Titan G2 80-200 at FEI Company (Hillsboro, OR) and an aberration corrected JEOL JEM 2100F/Cs scanning transmission electron microscope at UC Davis. All microscopes were operated at 200 kV. TEM specimens were imaged in an edge-on orientation, i.e., the $\langle 110 \rangle$ direction of the Si substrate was parallel to the incoming electron beam.

EDXS elemental distribution maps were acquired using the FEI Super-X EDX detector attached to a FEI Titan G2 80-200, which was installed at FEI Company. EELS line scans were acquired using a Gatan Tridiem spectrometer attached to the aberration corrected JEOL JEM 2100F/Cs instrument.

Crystalline orientation maps were used to study the crystalline orientation of Ni and Au grains along the interface. PED was performed using the JEOL JEM 2100F/Cs equipped with the NanoMEGAS Digistar hardware controlled by the Topspin™ precession control platform (AppFive LLC, Arizona). The step size was 1 nm with precession angle of 0.5° . Detailed information regarding the underlying physics of this technique are reported elsewhere [24–26].

The electron diffraction patterns were recorded from 25 different areas of one TEM sample. The width of the polycrystalline ring in each electron diffraction pattern was measured three times independently and calibrated using the simultaneously acquired silicon diffraction signal. The calculated lattice spacing was compared with tabulated values of bulk Ni to calculate strain. The stress was then determined based on the following equation: [27]

$$\sigma = \frac{E}{1-\nu} \times \varepsilon \quad (1)$$

$E= 200$ GPa is the elastic modulus of Ni, and $\nu=0.3$ is the Poisson ratio.

3. Results

Fig. 1a shows a cross-sectional TEM bright field micrograph of the bilayer film before annealing. A difference in image contrast can be observed between the top and bottom layers of the bilayer film, with the Ni layer having a brighter contrast than the Au layer (Fig. 1a). An abrupt change in contrast at the Ni/Au interface indicates no intermixing has occurred between Au and Ni before annealing. After annealing (Fig. 1b), re-arrangements of Au and Ni grains is observed throughout the metal film and separate Au and Ni layers can no longer be identified. Moreover, the film becomes semi-continuous, and the formation of holes and voids are observed. In some areas, indicated by an arrow, holes have formed in the annealed film and expose the underlying substrate. Slightly higher contrast at the substrate surface underneath the voids results from preferential thinning during FIB preparation.

The chemical distribution of the as-deposited film was further characterized with STEM-EELS line scans. Contrast in the ADF image in Fig. 2a shows the clear separation

of Au and Ni at the top and bottom of the film, respectively. Furthermore, a thin 2nm wide layer is observed to separate the Au and Ni layers (Fig. 2a). EELS line scans (Fig. 2b) acquired from the area observed in Fig 2a demonstrate an increase in the integrated oxygen K edge intensity at the Ni/Au interface, confirming the presence of a roughly 2nm wide native NiO layer at the Ni/Au interface.

The chemical distribution of the annealed film was characterized with STEM-EDXS mapping. Fig. 3a shows a STEM HAADF survey image that was used during spectrum acquisition. Fig. 3b and 3c display corresponding EDXS chemical distributions maps obtained from spectral intensities of the Ni $L\alpha_{12}$ (yellow) and Au $M\alpha_1$ (purple), respectively. The same color codes are used for subsequent plots of spectral intensities throughout the remainder of this manuscript. The result confirms the direct correlation of dark field image intensities with the presence (or respective absence) of Ni and Au, respectively. On the right side, as indicated by the red arrow in Fig 3a, both Ni and Au intensity co-exist in the EDXS mapping, which is likely to result from grain overlapping due to relatively smaller grain size.

In the region of interest, Au/SiO₂ occupies most of the interface with Ni grains sitting on top. A TEM analysis of a 10 μ m long section of the interface complemented by the characterization of 2 cross-sectional SEM samples revealed that roughly 54% of the film/substrate interface is comprised of Au/SiO₂, while only 21% shows a Ni/SiO₂ configuration. The remaining 25% of the substrate surface is exposed by either holes or voids in the film.

PED was used to acquire crystallographic information from the same area as Fig. 3. Phase maps were created by matching the acquired electron diffraction patterns with

calculated templates for Ni and Au at various different orientations. Phase maps were created using the Topspin software to determine the crystalline phase and orientation in each area of the film. In Fig. 4a, red areas in the phase map correspond to the Ni FCC phase, while yellow areas correspond to Au FCC phase. The derived phase map is in excellent agreement with the EDX composition maps, except at positions where the Au and Ni grains overlap. An orientation map was created using the PED patterns and is shown in Fig. 4b. The image contrast in Fig. 4b represents the crystallographic direction of the film, normal to the film/substrate interface. Each color corresponds to the directions observed in the inverse pole figure to the right of Fig. 4b. Within one phase, several colors were observed indicating multiple grains. Stacked Ni and Au grains, as marked in Fig. 4b, stay in the similar crystalline orientation around $\langle 853 \rangle$.

Texturing of the two metals in the annealed film was determined from the PED data using the harmonic extension method [28]. Fig. 5a and 5b show texture intensity plots along the interface normal, for Au and Ni grains, respectively. The presented inverse pole figures are considered representative as they were calculated from PED data obtained from a 6.5 μm long interface section including around 640 individual grains. Intensities in these inverse pole figures scale with the observed frequency of a given crystallographic orientation. Both Au and Ni show strong texture along the direction normal to the interface, with Au predominantly oriented along the $\langle 111 \rangle$ direction. Conversely Ni grains show texture around the $\langle 213 \rangle$ direction with a frequency 50% less than that for Au along the $\langle 111 \rangle$ direction. Ni is also observed to have some texture around the $\langle 111 \rangle$ and $\langle 001 \rangle$ directions. However, these orientations are $\sim 33\%$ less frequent than the $\langle 213 \rangle$ direction.

Figs. 6a and 6b show an ADF STEM and a bright field TEM micrograph of an interface between a Ni and Au grain after a void has formed at the Ni/Au/SiO₂ triple junction. Due to the difference in atomic number Ni and Au grains can clearly be distinguished from each other (cf. Fig. 6a). The bright field TEM image in Fig. 6b indicates a rather well-defined Au surface at the void, while the Ni surface has a more diffuse contrast.

EELS line profiles were acquired across the Ni grain from the area marked in Fig. 6a in the direction normal to the interface plane. Integrated spectral intensities for the Ni L_{2,3} and oxygen K edges are plotted as a function of relative distance in Fig. 7a. At the top surface of the Ni grain both the Ni L_{2,3} and oxygen K edge intensities begin to increase. Inside the Ni grain, the oxygen K-edge signal diminishes while the Ni signal continuously increases. Approaching the void the integrated oxygen K-edge signal reveals a strong signal with a full-width at half maximum (FWHM) around 8-10 nm. Inside the void both O and Ni signals become indistinguishable from noise. Si L_{2,3} edge was also detected at the bottom surface of the Ni grain as marked in Fig. 6a. Fig. 7b shows the background subtracted fine structure of the Si L_{2,3} edge acquired from the bottom surface, which is in excellent agreement with the near edge fine structure found in reference spectra for bulk SiO₂ [29]. From the results in Fig. 7 it is concluded that SiO₂ is present at the bottom surface of the Ni grain, adjacent to the void.

Void formation was also observed at Ni/Au phase boundaries inside the metal film. Fig. 8a shows a HAADF STEM survey image of an area where a void formed at the Ni/Au grain boundary. Figs. 8b and 8c display EDXS chemical distributions maps for Au and Ni, respectively. In Fig 8a, the nanostructure displays inclined grain boundaries

between Ni and Au, which divide the region of interest into three areas. Area 1 towards the left is comprised predominantly of Au, while area 3 on the right side of Fig. 8a is primarily composed of Ni. The central area, area 2, represents an overlap of Au and Ni rich phases along the viewing direction. In area 2, a region with darker contrast and a faceted shape is observed. The chemical distribution map for Au (Fig. 8b) reveals an absence of intensity in the same region, while the Ni distribution map shows only a slight decrease in intensity (Fig. 8c). These observations suggest that the faceted void is predominantly located inside the Au rich grain that may also extend slightly into the Ni rich grain.

The shape of the void shows mostly faceting of the adjacent metal phases, which is clearly observed by HRTEM (Fig. 9a). Some edges of the void reveal, however, slightly rounded shape. The lattice contrast observed inside the void originates from the Ni rich phase located in the same field of view due to the projection mode for TEM imaging. Moiré contrasts surrounding the void confirm that Au and Ni grains overlap along the viewing direction, while the absence of Moiré patterns is expected from a void which is directly in front of or behind the Ni rich grain. The void shape was calculated using the Wulffmaker software [30], based on the assumption that the void obeys the same Wulff shape as Au particles. The orientation of Au crystal was obtained from the precession assisted diffraction patterns. The free surface energy of (100), (110), and (111) planes for Au were extracted from references [35] (see Table 1) and used for modeling. Overall the projected outline of the calculated void shape (Fig. 9b) is overlaid on the HRTEM micrograph (Fig. 9a) and agrees surprisingly well with the experimentally observed geometric shape.

4. Discussion

4.1 Film morphology at the early stages of dewetting

In the as-deposited metal bilayer film, the Ni and Au layers are polycrystalline, continuous and uniform in thickness. Cross-sectional EELS line scans reveal a 2-3 nm continuous native NiO_x layer formed between Ni and Au, which formed as a surface oxide on the top of the Ni film prior to Au deposition. The oxide layer likely obstructs inter-diffusion of Au and Ni at low temperatures while cross-sectional TEM and STEM imaging reveals that at elevated temperatures inter-diffusion eventually occurs. Figs 3 and 4 demonstrate that in some areas Au has diffused underneath the Ni film to replace the Ni/SiO₂ interface by the Au/SiO₂ interface. Similar observations were reported previously for the annealing of 5 nm thick Au films on top of 10 nm Ni films in air [31]. Chen et al. have argued that the driving force in this case was the difference of oxygen affinity between Ni and Au. In this study, however, annealing was carried out in vacuum, i.e., at an O₂ partial pressure of 7×10⁻⁸ torr. The interface energies for Au/SiO₂ and Ni/SiO₂ can be estimated by the following equation [32]:

$$\gamma_{film/substrate} = \gamma_{film/vapor} + \gamma_{substrate/vapor} - W_{adhesive} . \quad (2)$$

The work of adhesion $W_{adhesive}$ for Ni and Au on SiO₂, and the surface energies γ for Ni, Au and SiO₂ were taken from references [33-38] and are listed in Table 1. From the reference values, interface energies were calculated for Au/SiO₂ and Ni/SiO₂ configurations, and listed in Table 1. Due to the anisotropic nature of Au and Ni surface energies, the calculated interface energies strongly depend on the orientation of the respective metal film. The difference of interface energy between two different types of interface is within 0.3 J/m², which is similar to the difference between calculated [35] and

experimentally determined free surface energies values [36, 37] (see Table 1). In addition, it must be noted that the values for the work of adhesion extracted from reference 34 were determined by fracture measurements that include irreversible processes such as plastic deformation [39]. Hence, the Au/SiO₂ or Ni/SiO₂ interface energies listed in Table 1 do not provide conclusive evidence for which interface configuration is energetically favorable.

The PED analysis of annealed bilayer films has demonstrated that Au grains are highly textured around $\langle 111 \rangle$, while Ni grains reveal $\langle 213 \rangle$ orientation parallel to the substrate's interface normal. The (213) free surface energy for Ni is higher than the lower-index Ni surface energies listed in Table 1 [40]. According to equation (2) Ni (213) planes in contact with the underlying SiO₂ therefore have a higher interface energy compared to lower-indexed Ni/SiO₂ interfaces. Analysis of electron diffraction patterns furthermore revealed that the polycrystalline as-deposited Ni film was under 0.79 ± 0.17 GPa compressive stress caused by the sputter deposition process at room temperature. Under this circumstance the as-deposited Ni/SiO₂ interface energy is considered even higher than suggested by Table 1 [41]. Therefore, it is concluded that the driving force for Au diffusion underneath the previously continuous Ni film is the lowering of the metal/SiO₂ interface energy. The formation of the Au/SiO₂ interface contributes in delaying thin film agglomeration of the bilayer film, in conjunction with the previously observed alloying effects.

Ni grains are also expected to obtain a $\langle 111 \rangle$ texture similar to Au. Kinetics, however, have a significant effect on the rearrangement of Ni and Au at the early stage of film agglomeration. Free surface diffusion of Ni was suppressed by both the NiO and Au

layers, and, therefore, obstructed grain boundary grooving. In addition, the diffusivity of Au is significantly larger than that of Ni [42], which promotes Au migration as the kinetically dominant mechanism to facilitate the minimization of the metal/substrate interface energy.

The ADF-STEM micrograph in Fig. 10 shows a boundary between two adjacent Ni grains. Under the respective imaging conditions, bright intensities represent Au, while lower intensities signify Ni. The grain boundary exhibits a sharp bright image intensity, indicating that Au diffused along the grain boundary during annealing, forming a Au rich grain underneath the two Ni grains. The diffuse bright intensity in the Ni grains, near the grain boundary, may also indicate residual Au-Ni alloying that occurred at elevated temperatures. As the temperature increases, the contribution of bulk self-diffusion increases [43], as well as the amount of Au-Ni alloying. Hence, Au may also diffuse through Ni grains towards the substrate surface and form an Au/SiO₂ interface. Both mechanisms lead to the formation of the observed Au/SiO₂ interface driven by the reduction of total interface energy. The observed sub-stoichiometric nickel oxide layer between the as-deposited metal layers revealed no significant influence on the morphological changes of the metal film upon thermal annealing.

Electron diffraction pattern analysis has revealed that the polycrystalline Ni film was under compressive stress due to sputter deposition. It is, therefore, concluded that the Au/SiO₂ interface energy is lower than that for a Ni/SiO₂ interface configuration given that the Ni film is under compressive stress [41]. The experimental observations suggest that Au diffusion outruns relaxation of the Ni film and, therefore, forms a predominant Au/SiO₂ interface. Surprisingly, no remaining Au absorption layers on top of

agglomerated Ni grains were detected by either EDXS elemental mapping or atomic resolution HAADF-STEM imaging.

4.2 Void nucleation

Voids were predominantly observed at Ni/Au/SiO₂ triple junctions. Void formation at the Ni/SiO₂ interface during thermal annealing was previously observed [44], and the compressive stress of the as-deposited Ni layer may have caused delamination through buckling [45]. HRTEM imaging combined with EELS characterization has revealed a NiO layer at the Ni/void interface in Fig 6, while some SiO₂ was also detected in the same area. The same EELS characterization was conducted for the Au grain on the opposite side of the phase boundary, but no Si L_{2,3} signal was detected. These observations may indicate partial delamination, i.e., buckling, of the as-deposited Ni film due to compressive stress in addition to local void formation. The interfacial fracture energy for Ni/SiO₂ is higher than that for Au/SiO₂ (1.37 J/m² vs. 0.39 J/m² respectively [33, 34]), which is consistent with this interpretation.

The observation of voids predominantly at Ni/Au/SiO₂ triple junctions suggests that voids were formed after the rearrangement of Ni and Au. Evidence of void nucleation and grain boundary grooving for Au/Ni bilayers was previously discovered by cross-sectional SEM imaging [17]. In this cross-sectional TEM study, however, only the formation of voids was observed. During the rearrangement of Ni and Au, the difference in the interdiffusion coefficient of Au and Ni could induce a high density of vacancies in the film. Moreover, alloying and the formation of Au/Ni grain boundaries could also cause stress due to a large lattice mismatch of 15% [46]. As a consequence, void nucleation was found to be the dominant mechanism of hole formation during the early

stages of the dewetting process. It must be noted that the top Au layer may have started to dewet early during annealing due to its higher diffusivity and large surface area. More extensive in-situ TEM studies would be required to provide additional evidence, but is beyond the scope of this publication.

Besides the void nucleation at Ni/Au/SiO₂ triple junction, Kirkendall void formation was also observed at Ni/Au phase boundaries. According to the phase diagram, intermixing of 21% Ni in Au, and 9% Au in Ni occurs at 675°C. The diffusivity of Au in Ni is, however, higher than that for Ni in Au. Thus, the Kirkendall effect [47] causes void formation at the phase boundary but within the Au phase. In this study, voids around Au/Ni grain boundaries were located to be predominantly within the Au phase (cf. Fig. 8). Kirkendall voids likely act as a source of vacancies during dewetting, aiding in the formation of voids which are caused by capillary instabilities at metal/grain boundary/substrate triple junctions [48, 49]. Furthermore, Kirkendall voids create Au/Ni/Void triple junctions, where new voids can begin to nucleate. To our knowledge, Kirkendall voids have not been previously observed during the dewetting of bilayer films.

Faceting of the void inside the Au phase was observed due to the anisotropic surface energy of solid Au [36]. The surprising agreement of the Wulff constructed shape of the void with the experimental observations (cf. Fig 9a) indicates that the void and Au grains are approaching thermodynamic equilibrium. Observed differences between experimentally observed and modeled void shapes must origin from the intersecting Au/Ni grain boundary, and the fact that thermodynamic equilibrium has not yet been reached. The rather complicated morphology of the annealed bilayer film indicates, however, that the agglomeration process to form homogeneous interface structures that

correspond to the lowest energy configuration is hindered due to local intermixing of Ni and Au at elevated temperatures.

Conclusion

The agglomeration of Au/Ni bilayer films on SiO₂/Si substrates was studied in detail by cross-sectional TEM techniques. The observations revealed considerable changes in film morphology, chemical distribution, formation of texture, and void nucleation at triple points and Au/Ni phase boundaries. Au diffused underneath the Ni film during the annealing of the as-deposited bilayer film, reduce the metal/SiO₂ interface energy by relieving the considerable compressive stress in the Ni film. The Au grains were able to achieve a <111> texture due to the high mobility of Au, forming a more energetically favorable metal/SiO₂ interface compared with the higher indexed Ni grains. Formation of the Au/SiO₂ interface delays the agglomeration of the bilayer film, in conjunction with the previously observed alloying effect. Void formation is observed to be the dominant mechanism for the nucleation of holes during the early stages of film agglomeration. Besides nucleation at film/substrate triple junctions, the Kirkendall effect was observed to cause the formation of voids at Au/Ni phase boundaries, with voids forming inside the Au phase. The formation of Kirkendall voids is another consequence of Au-Ni alloying which affects the agglomeration process in Au/Ni bilayer films.

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Reference

- [1] W.D. Kaplan, D. Chatain, P. Wynblatt, W.C. Carter. A review of wetting versus adsorption, complexions, and related phenomena: the rosetta stone of wetting, *J Mater Sci* 48 (2013) 5681-5717.
- [2] J.W. Cahn, J.E. Hilliard. Free Energy of a Nonuniform System .1. Interfacial Free Energy, *J Chem Phys* 28 (1958) 258-267.
- [3] D. Deduytsche, C. Detavernier, R.L. Van Meirhaeghe, C. Lavoie. High-temperature degradation of NiSi films: Agglomeration versus NiSi₂ nucleation, *J Appl Phys* 98 (2005).
- [4] L. Kondic, J.A. Diez, P.D. Rack, Y.F. Guan, J.D. Fowlkes. Nanoparticle assembly via the dewetting of patterned thin metal lines: Understanding the instability mechanisms, *Phys Rev E* 79 (2009).
- [5] J. Yun, R. Wang, W.K. Choi, J.T.L. Thong, C.V. Thompson, M. Zhu, Y.L. Foo, M.H. Hong. Field emission from a large area of vertically-aligned carbon nanofibers with nanoscale tips and controlled spatial geometry, *Carbon* 48 (2010) 1362-1368.
- [6] J. Guan, B. Yu, L.J. Lee. Forming highly ordered arrays of functionalized polymer nanowires by dewetting on micropillars, *Adv Mater* 19 (2007) 1212-1214.
- [7] W.W. Mullins. Theory of Thermal Grooving, *J Appl Phys* 28 (1957) 333-339.
- [8] C.M. Kennefick, R. Raj. Copper on Sapphire - Stability of Thin-Films at 0.7-Tm, *Acta Metallurgica* 37 (1989) 2947-2952.
- [9] C.V. Thompson. Solid-State Dewetting of Thin Films, *Annu Rev Mater Res* 42 (2012) 399-434.
- [10] C. Manuela Müller, R. Spolenak. Dewetting of Au and AuPt alloy films: A dewetting zone model, *J Appl Phys* 113 (2013) 094301.
- [11] J. Petersen, S.G. Mayr. Dewetting of Ni and NiAg solid thin films and formation of nanowires on ripple patterned substrates, *J Appl Phys* 103 (2008) 023520.
- [12] Y. Kwon, N.H. Kim, G.P. Choi, W.S. Lee, Y.J. Seo, J.S. Park. Structural and surface properties of NiCr thin films prepared by DC magnetron sputtering under variation of annealing conditions, *Microelectron Eng* 82 (2005) 314-320.
- [13] D. Amram, L. Klinger, E. Rabkin. Anisotropic hole growth during solid-state dewetting of single-crystal Au-Fe thin films, *Acta Mater* 60 (2012) 3047-3056.

- [14] M. Perzanowski, Y. Zabala, J. Morgiel, A. Polit, M. Krupinski, A. Dobrowolska, M. Marszalek. AFM, XRD and HRTEM Studies of Annealed FePd Thin Films, *Acta Phys Pol A* 117 (2010) 423-426.
- [15] J.H. Wang, X.G. Lu, B. Sundman, X.P. Su. Thermodynamic assessment of the Au-Ni system, *Calphad* 29 (2005) 263-268.
- [16] D. Wang, P. Schaaf. Ni-Au bi-metallic nanoparticles formed via dewetting, *Mater Lett* 70 (2012) 30-33.
- [17] A. Herz, D. Wang, T. Kups, P. Schaaf. Solid-state dewetting of Au/Ni bilayers: The effect of alloying on morphology evolution, *J Appl Phys* 116 (2014).
- [18] A. Herz, D. Wang, R. Muller, P. Schaaf. Formation of supersaturated Au-Ni nanoparticles via dewetting of an Au/Ni bilayer, *Mater Lett* 102 (2013) 22-25.
- [19] A. Herz, M. Friak, D. Rossberg, M. Hentschel, F. Theska, D. Wang, D. Holec, M. Sob, O. Schneeweiss, P. Schaaf. Facet-controlled phase separation in supersaturated Au-Ni nanoparticles upon shape equilibration, *Appl Phys Lett* 107 (2015).
- [20] A.M. Thron, P.K. Greene, K. Liu, K. van Benthem. Structural changes during the reaction of Ni thin films with (100) silicon substrates, *Acta Mater* 60 (2012) 2668-2678.
- [21] D. Chatain, V. Ghetta, P. Wynblatt. Equilibrium shape of copper crystals grown on sapphire, *Interface Sci* 12 (2004) 7-18.
- [22] M. Schaffer, B. Schaffer, Q. Ramasse. Sample preparation for atomic-resolution STEM at low voltages by FIB, *Ultramicroscopy* 114 (2012) 62-71.
- [23] C.A. Volkert, A.M. Minor. Focused ion beam microscopy and micromachining, *MRS Bulletin* 32 (2007) 389-399.
- [24] R. Vincent, P.A. Midgley. Double Conical Beam-Rocking System for Measurement of Integrated Electron-Diffraction Intensities, *Ultramicroscopy* 53 (1994) 271-282.
- [25] J.G. Brons, G.B. Thompson. Orientation Mapping via Precession-Enhanced Electron Diffraction and Its Applications in Materials Science, *Jom-Us* 66 (2014) 165-170.
- [26] A. Avilov, K. Kuligin, S. Nicolopoulos, M. Nickolskiy, K. Boulahya, J. Portillo, G. Lepeshov, B. Sobolev, J.P. Collette, N. Martin, A.C. Robins, P. Fischione. Precession technique and electron diffractometry as new tools for crystal structure analysis and chemical bonding determination, *Ultramicroscopy* 107 (2007) 431-444.
- [27] M. Meyers, K. Chawla. *Mechanical Behavior of materials*. Cambridge University Press, New York, 2009.
- [28] H.J. Bunge, *Texture Analysis in Materials Science: Mathematical Methods*. Butterworths, London, 1982

- [29] C.C. Ahn, P. Rez. Inner Shell Edge Profiles in Electron-Energy Loss Spectroscopy, *Ultramicroscopy* 17 (1985) 105-115.
- [30] R.V. Zucker, D. Chatain, U. Dahmen, S. Hagege, W.C. Carter. New software tools for the calculation and display of isolated and attached interfacial-energy minimizing particle shapes, *J Mater Sci* 47 (2012) 8290-8302.
- [31] L.C. Chen, F.R. Chen, J.J. Kai, L. Chang, J.K. Ho, C.S. Jong, C.C. Chiu, C.N. Huang, C.Y. Chen, K.K. Shih. Microstructural investigation of oxidized Ni/Au ohmic contact to p-type GaN, *J Appl Phys* 86 (1999) 3826-3832.
- [32] M. Ohring, *Materials Science of Thin Films*, Second ed. Academic Press, Waltham, 2001
- [33] M.S. Kennedy, N.R. Moody, D.P. Adams, M. Clift, D.F. Bahr. Environmental influence on interface interactions and adhesion of Au/SiO₂, *Mat Sci Eng a-Struct* 493 (2008) 299-304.
- [34] C.H. Lee, J.H. Kim, C.Y. Zou, I.S. Cho, J.M. Weisse, W. Nemeth, Q. Wang, A.C.T. Van Duin, T.S. Kim, X.L. Zheng. Peel-and-Stick: Mechanism Study for Efficient Fabrication of Flexible/Transparent Thin-film Electronics, *Sci Rep-Uk* 3 (2013).
- [35] E.A. Holm, D.L. Olmsted, S.M. Foiles. Comparing grain boundary energies in face-centered cubic metals: Al, Au, Cu and Ni, *Scripta Mater* 63 (2010) 905-908.
- [36] H.P. Bonzel, M. Nowicki. Absolute surface free energies of perfect low-index orientations of metals and semiconductors, *Physical Review B - Condensed Matter and Materials Physics* 70 (2004) 1-9.
- [37] H. Meltzman, D. Chatain, D. Avizemer, T.M. Besmann, W.D. Kaplan. The equilibrium crystal shape of nickel, *Acta Materialia* 59 (2011) 3473-3483.
- [38] J. Bohm. *Treatise on solid state chemistry*. Plenum Press, New York 1975.
- [39] J. Kim, K.S. Kim, Y.H. Kim. Mechanical effects in peel adhesion test, *journal of Adhesion Science and Technology* 3 (1989) 175-187.
- [40] Y.N. Wen, H.M. Zhang. Surface energy calculation of the fcc metals by using the MAEAM, *Solid State Commun* 144 (2007) 163-167.
- [41] T. Frolov and Y. Mishin, Thermodynamics of coherent interfaces under mechanical stress. I. Theory, *Phys. Rev. B* 85 (2012) 224106.
- [42] M.J.H. van Dal, M.C.L.P. Pleumeekers, A.A. Kodentsov, F.J.J. van Loo. Diffusion studies and re-examination of the Kirkendall effect in the Au-Ni system, *J Alloy Compd* 309 (2000) 132-140.
- [43] A. Kosinova, D. Wang, P. Schaaf, O. Kovalenko, L. Klinger, E. Rabkin. Fabrication of hollow gold nanoparticles by dewetting, dealloying and coarsening, *Acta Mater* 102 (2016) 108-115.

- [44] A.M. Thron, P. Greene, K. Liu, K. van Benthem. In-situ observation of equilibrium transitions in Ni films; agglomeration and impurity effects, *Ultramicroscopy* 137 (2014) 55-65
- [45] J.A. Thornton, D.W. Hoffman. Stress-Related Effects in Thin-Films, *Thin Solid Films* 171 (1989) 5-31.
- [46] Y. Gao, K.L. Merkle. High-Resolution Electron-Microscopy of Metal Metal and Metal Metal-Oxide Interfaces in the Ag/Ni and Au/Ni Systems, *J Mater Res* 5 (1990) 1995-2003.
- [47] H.J. Fan, M. Knez, R. Scholz, D. Hesse, K. Nielsch, M. Zacharias, U. Gosele. Influence of surface diffusion on the formation of hollow nanostructures induced by the Kirkendall effect: The basic concept, *Nano Lett* 7 (2007) 993-997.
- [48] P.R. Gadkari, A.P. Warren, R.M. Todi, R.V. Petrova, K.R. Coffey. Comparison of the agglomeration behavior of thin metallic films on SiO₂, *J Vac Sci Technol A* 23 (2005) 1152-1161.
- [49] E. Shaffir, I. Riess, W.D. Kaplan. The mechanism of initial de-wetting and detachment of thin Au films on YSZ, *Acta Mater* 57 (2009) 248-256.

Figure Captions

Figure 1: Cross-sectional TEM bright field micrographs of the (a) as-deposited bilayer film and (b) the annealed bilayer film. The red arrow highlights the formation of a hole.

Figure 2: (a) An annular dark field image of as-deposited film. (b) The integrated EELS intensities of the oxygen K plotted as a function of relative position across bilayer film, from the arrow marker by the red arrow in (a)

Figure 3: EDXS chemical distribution maps and the corresponding STEM survey image. (a) The HAADF STEM survey micrograph. (b) and (c) are EDXS chemical distribution maps obtained from the spectral intensities of the Ni $L\alpha_{1,2}$ (yellow) and Au $M\alpha_1$ (purple), respectively.

- Figure 4: (a) Phase map calculated from PED. Red intensity signifies the Ni FCC phase while yellow intensities signify the Au FCC phase. (b) Orientation map for the direction normal to the interface with the color intensities corresponding to the inverse pole figure to the right of the image.
- Figure 5: Texture intensity plot in the format of inverse pole figure of (a) Au and (b) Ni, respectively.
- Figure 6: (a) STEM and (b) bright field TEM micrographs of an interface between a Ni and Au grains, where a void has formed underneath the phase boundary.
- Figure 7: (a) Plots of integrated EELS intensities for the Ni $L_{2,3}$ and O K edge as a function of relative position across the Ni grain, as marked in Fig. 6a by the red arrow. (b) Si $L_{2,3}$ edge recorded from the bottom area of Ni as marked by the red dot in Fig. 6a, plotted in comparison to a reference spectrum for bulk SiO_2 [29].
- Figure 8: EDXS chemical distribution maps and corresponding STEM survey image. (a) The HAADF STEM survey micrograph. (b) and (c) are EDXS chemical distribution maps obtained from spectral intensities of the Au $M\alpha_1$ (purple) and Ni $L\alpha_{1,2}$ (yellow), respectively. The dashed lines highlight areas where Ni and Au grains overlap. The dashed circle highlights a void observed in projection.
- Figure 9: (a) The HRTEM micrograph of the void observed in Fig. 8. (b) The simulated void with the orientation obtained from the PED. The frame of facet planes are cropped from simulated void (b) and matched with the one in HRTEM micrograph, as shown by the dashed red lines in (a)

Figure 10: Annular dark field micrograph showing the presence of Au at a Ni grain boundary, and the formation of a Au grain underneath the two Ni grains.

Tables

Table 1: Surface energy, adhesive energy and calculated interface energy for Ni and Au with SiO₂. All values in J/m²

Energy	Au	Ni
Adhesive energy w SiO ₂	0.39 ^[33]	1.37 ^[34]
Surface energy(cal) (100) ^[35]	1.176	2.06
Surface energy(cal) (110) ^[35]	1.282	2.375
Surface energy(cal) (111) ^[35]	1.094	1.953
Surface energy(exp) (111)	1.46 ^[36]	2.05 ^[37]
Interface energy (100) w SiO ₂	1.093	0.997
Interface energy (110) w SiO ₂	1.199	1.312
Interface energy (111) w SiO ₂	1.011	0.89
SiO ₂ free surface energy: 0.307 ^[38]

(a) Au texture

(b) Ni texture