Agglomeration and long-range edge retraction for Au/Ni bilayer films during thermal annealing

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Abstract

The solid state dewetting of Au/Ni bilayer films from SiO₂/Si substrates exhibits both homogeneous and localized dewetting of Ni and long-edge retraction for Au under isothermal annealing condition. The top Au layer retracted up to 1 mm from the edge of the substrate wafer to reduce the energetically unfavored Au/Ni interface. In contrast, Ni dewetted and agglomerated locally due to its limited diffusivity compared to Au. Film morphology and local chemical composition varied significantly across hundreds of micrometers along the direction normal to the retracting edge. The accumulation of Au from long-range edge retraction resulted into the separation of Au and Ni, which are affected by alloying between the two elements. The experimental observations suggest that alloying combined with unequal self-diffusion coefficient for the metal components control the bilayer dewetting process.

Keywords: bilayer film; dewetting; edge retraction; agglomeration; annealing; thin film; SEM

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Introduction

Thin films deposited at low temperatures are typically kinetically constrained and agglomerate when heat treated. Such process, often referred to as dewetting [1], is a result of an imbalance between interface and surface free energies for as-deposited thin films[2]. Solid state dewetting can be a serious concern in microelectronics reliability[3], while it is utilized for engineering of nanostructures with potential applications in energy storage[4], catalysis[5], optical applications[6], and magnetic recording media [7,8]. Mechanisms for dewetting of single layer films have been studied extensively. Break-up of polycrystalline films is often initiated by grain boundary grooving, where grain boundaries intersect the free surface of the film[9-11]. Surface diffusion of atoms away from the grain boundary forms grooves and ridges on the surface of the film. Continuous grooving leads to the formation of holes. Alternatively, instabilities at triple junctions between the grain boundaries in the film and the film/substrate interface can cause void formation and growth [12-14]. Once the void reaches the free surface of the film, a hole is formed, which ultimately leads to film agglomeration. Barring any defects within the substrate surface, dewetting of single component polycrystalline films initiates and develops homogeneously across the surface, resulting in inhomogeneous distributed arrays of individual islands [15].

Agglomeration of kinetically constrained bilayer or alloyed thin films is expected to strongly depend on the interaction between the different components. However, only few studies on multi-component thin films are reported in the literature. Alloying of Au films with small amounts of Pt was shown to delay the onset of dewetting at low temperatures[16]. However, mechanisms that determine the observed kinetics of dewetting were not confirmed. Dewetting of Ni-Ag alloyed films[17] revealed that the addition of immiscible Ag in Ni causes fractal-like

growth of holes rather than the expected capillarity driven nucleation and growth of holes initiated by grain boundary grooving. For alloyed Ni-Cr films [18] different annealing conditions were reported to result in a variety of dewetting kinetics due to surface oxidation and film-substrate interaction because of differences in the oxygen affinity for the two metals. Nanosecond pulsed laser melting induced dewetting of Ag/Co [19] bilayer films due to spinodal instabilities, which were caused by concentration gradients as a function of film deposition sequence and solubility. In contrast, Au/Fe and Fe/Pd bilayer films show enhanced thermal stability upon annealing due to alloying effects [20, 21].

Au and Ni were chosen as components for bilayer films due to their homogeneous solid solution for temperatures above 816°C, while a large miscibility gap spanning the whole composition range below 100°C [22]. Early dewetting studies of Au/Ni bilayer films in argon ambient revealed that the morphology of dewetted islands varies at different annealing temperatures due to differences in solubility [23, 24]. Enhanced solubility above 700°C results in the formation of an intermediate phase that affects the kinetics of hole formation [25]. Supersaturated Au-Ni particles with sizes below 1 μm can form when a Ni/Au bilayer film is annealed at temperatures above the miscibility gap. Phase separation from supersaturated Au-Ni particles revealed Ni-rich phases with $\langle 100 \rangle$ facets due to a minimization of elastic energy at the interface between the Ni and Au rich phases [26].

Previous studies mostly assumed that dewetting initiates locally by grain boundary grooving at the exposed surface of the top film or void formation at metal/substrate interface, and occurs homogeneously over large interface areas [15]. Mass transport over larger length scales with changes in chemical composition as a function of edge retraction were not considered. Long-range edge retraction was only reported for single crystalline Ni film spanning distances below 5

μm [27]. In this study, however, we discovered heterogeneous film morphology and re-arrangement of agglomerated metal islands coupled with long-range edge retraction during thermal annealing of thin Au/Ni bilayer films. Topographical and chemical contrast imaging by scanning electron microscopy (SEM) was used in combination with energy dispersive X-ray spectroscopy (EDXS). The experimental observations suggest that the bilayer dewetting process is strongly affected by alloying and unequal self-diffusion coefficient for the metal components.

Experimental Details

Nickel and gold films were consecutively deposited onto Si substrates each with a nominal thickness of 30 nm (Fig 1a). Prior to metal film deposition a 12 nm SiO_2 layer was thermally grown on the (100) surface of silicon substrates to avoid silicide formation [28]. Ni films were deposited at room temperature by DC magnetron sputtering at 100 W power, a base pressure of $2.3 \times 10^{-6} \text{ Pa}$, and an atmosphere of 0.27 Pa argon. The resulting sputter rate was 0.14 nm/s. Au films were deposited afterwards on top of Ni at room temperature using a Denton vacuum desk II cold sputtering unit. Au deposition was performed at a base pressure of 2.7 Pa, an atmosphere maintained at 10 Pa, and 3 W, thus resulting in sputtering rates around 0.25 nm/s. Before inserting into the deposition chamber the SiO_2/Si substrates were cleaned by sonication in deionized water and methanol. Fig. 1a shows a sketch view of the as-deposited interface configuration.

The as-deposited films were annealed for 1 hour in a three-zone vacuum tube furnace (Lindberg) at 675°C and a base pressure of $8 \times 10^{-4} \text{ Pa}$. To avoid contamination, the samples were placed in an alumina boat during annealing. Fast heating and cooling were accomplished by pushing and withdrawing the quartz tube into and out of the hot zone of the furnace [29].

The morphology and structure of annealed samples were characterized with a FEI Scios dual-beam instrument (FEI Company, Hillsboro, OR) equipped with both Everhart-Thornley detector

(ETD) and Trinity detector system[30]. The latter consists of a through-the-lens detector (T1) and through-the-column detector (T3) to collect backscattered electrons (BSE) and secondary electrons (SE), respectively. Chemical composition profiling was carried out by energy-dispersive X-ray spectroscopy (EDXS) with an Oxford X-Max 50 detector system attached to the same microscope.

Samples for cross-sectional SEM imaging were prepared by focused ion beam (FIB) sectioning. Initially a carbon protective layer with nominal thickness of 500 nm was deposited, assisted by 30 kV Ga^+ FIB with a beam current of 0.3 nA. Thereafter, ion-beam assisted deposition was continued at the same voltage but with higher ion beam current (3 nA) until a total nominal thickness of 2 μm was obtained. FIB sectioning was used to etch a trench on one side of the protective layer to allow cross-sectional imaging with a stage tilt of 52° with respect to the optical axis of the electron beam optics. Trenching was carried out at 30 kV and ion beam currents of 15 nA, followed by milling at 1 nA to reduce damage layers caused by the beam.

Results

The morphology of the annealed bilayer film was characterized using optical microscopy and SEM. Fig. 1b shows a plan view optical micrograph of the sample after annealing. The bilayer film appears mostly continuous in the center, while the edge retracted from two corners of the substrate wafer. Light reflected from receding edge appears bright yellow. Fig. 1c and 1d show SEM images of the sample surface obtained from the areas marked in Fig. 1b and 1c, respectively. The images were taken with the ETD detector and contain contributions from both BSE and SE signals. Seven regions with different morphology are observed and are labeled P1 to P7. P1 represents the largest area with rather homogeneous contrast under the respective imaging

conditions. P2 and P3 exhibit 10 μm wide bands with bright contrast, and a parallel 2-3 μm wide band with relatively dark contrast, respectively. Approaching the top right edge of the wafer (cf. Fig. 1b) SEM image contrast becomes brighter while the film reveals increasing roughness from P4 through P6. Large grains with relatively bright contrast are observed in P5, while in P6 the previously continuous film appears discontinuous, hence exposing the SiO_2/Si substrate with minimal image intensity. P7 is the edge of the wafer where arrays of individual metal islands are observed.

Cross-sectional SEM micrographs of the film/substrate interface were recorded with the ETD detector and are shown in Fig. 2a. The top layer with dark grey contrast represents the carbon protective layer deposited during FIB preparation, while the bright thin layer identifies the metal films. The relatively dark contrast below the metal film results from the Si substrate. The cross-sectional observations confirm the film morphology observed in Fig. 1b-d. Variations of film thickness are observed from P1 to P7, and were determined from SEM images acquired at a higher magnification under the same operating conditions (cf. Table 1). In P1 and P2 the thickness of the film is roughly 70-80 nm, which is slightly higher than the as-deposited nominal film thickness of 2x 30 nm. In P3 the thickness increases abruptly to approximately 210 nm. From P4 to P6 the film thickness further increases gradually to values as high as 530 nm. Strong variations of film thickness are observed in P5 and P6 due to Au agglomeration. No film thickness is provided for P7 as the bilayer metal film is no longer continuous.

Table 1 Thickness of the annealed film from region P1 to P6

Region	P1	P2	P3	P4	P5	P6
Width (nm)	70-80	70-80	210	160-210	235-530	235-530

The phase distribution of different areas within the dewetted film was further investigated using backscattered electrons recorded with the T1 detector [30], at a higher magnification (see Fig. 2b-d). The brightest contrast levels indicate Au-rich phases, intermediate grey contrasts represent Ni-rich phases, and dark contrast results from the exposed SiO₂/Si substrate. Some intermixing between Ni and Au is expected during annealing [22]. Throughout the remainder of the manuscript and unless explicitly stated, references to individual phase or grains will, therefore, always imply the major component with the minor component partially alloyed. Au-rich phase and Ni-rich phase chemical contrast observed in Fig. 2b-d shows significant variation in chemical distribution from the center (P1) to the edge of the substrate wafer (P7). Fig. 2b shows areas from P1 through P4 with Au and Ni contrast coexisting without significant dominance of one phase over the other. According to the BSE contrast P2 and P3 appear to be Au-rich and Ni-rich, respectively. In P4, Ni and Au contrast are coexisting similar to P1, but with coarser grains. However, the average contrast in P4 is darker compared to P1, suggesting slight enrichment of Ni compared to P1. In area P5 (Fig 2c), considerably larger grains with bright contrast indicate preferred agglomeration of Au, while P6 represents a transition region in which the bilayer film is partly ruptured. In P7 Ni is completely agglomerated and has formed individual islands on the substrate surface. Only small amounts of Au (brighter image contrast) were observed randomly distributed either in direct contact with the substrate or in the vicinity of Ni islands. The size of Ni islands in P7 is generally larger than in P6.

The chemical distribution from the center to the edge of the substrate wafer was further confirmed by EDXS. Fig. 3a shows a survey image that was used during spectrum acquisition, with the vertically integrated spectral intensities for each element plotted as a function of relative distance. Corresponding EDXS chemical distributions maps displayed in Fig. 3b-d, are obtained from spectral intensities of the Ni $L\alpha_{12}$ (red), Au $M\alpha_1$ (yellow), and Si $K\alpha_1$ (blue) lines, respectively. The same color codes are used for subsequent plots of spectral intensities throughout the remainder of this manuscript. In P1 spectral intensities reveal a rather homogeneous distribution of Au and Ni. Quantitative analysis in P1 using the Oxford Aztec software package with K-factor analysis and correction based on the effects of atomic number, adsorption, and fluorescence [31] reveals an average composition of 61.6 ± 0.2 at.% Ni and 38.4 ± 0.3 at.% Au. The experimental results are in excellent agreement with predicted values of 61 at.% for Ni and 39 at.% for Au derived from the nominal film thicknesses and physical densities. In P2 the intensity of Ni drops significantly, while spectral intensities for Si and Au increase, consistent with BSE imaging results (cf. Figure 2b). At the interface between P2 and P3 the intensity of Au drops abruptly while Si intensities show a sharp increase, indicating the formation of holes at the interface. In the narrow area P3, Ni intensities assume maximal values while the Au spectral intensities reveal a local minimum, confirming P3 consists predominantly of Ni. Entering region P4, the spectral intensities for Si and Ni drop abruptly and continue to gradually decrease throughout P4 and P5. In contrast, the integrated Au intensity rises rapidly at the P3/P4 interface and continues to gradually increase throughout P4. In P5 the spectral intensities for Au remain constant. Furthermore, the Au spectral intensity is greatest in P5, which correlates with the yellow colors observed in the optical image in Fig. 1b. Upon entering region P6, the Au intensities drop again abruptly, and continue to rapidly decay until the Au signal is

indistinguishable from detector noise in P7. Ni intensities continue to slowly decay throughout P6 and P7, while recorded Si intensities rapidly increase. The integrated EDXS intensities suggest an increasing area of exposed substrate in P6 and P7 and the retraction of Au away from the same areas.

Fig. 4 demonstrates typical film morphology and topography observed by BSE (Fig. 4a) and SE (Fig. 4b) imaging in region P1. Bright and dark intensities represent Au-rich and Ni-rich phases, respectively, and reveal agglomerated Ni grains embedded in a matrix of polycrystalline Au. Small contrast variations between individual Au grains are likely due to orientation-dependent BSE signals. The average size of both Au and Ni grains is around 200 nm. Fig. 4b shows that Ni phases reveal some topographical changes while the Au-rich matrix appears relatively smooth. Few holes are observed in the film, as demonstrated by small isolated areas with almost black intensity. Grain boundaries in the Au-rich matrix are observed as almost straight dark lines and varying width, indicating various degrees of grain boundary grooving. Some grain boundary grooves exhibit bright spot-like contrasts that indicate the presence of Au nanoparticles[30].

SEM images of areas P1 through P3 reveal clearly distinguishable film morphologies for the different regions (Fig. 5). Holes in the metal film are observed in all three areas with the largest holes located in P2 (cf. Fig. 5c and d). A preferential agglomeration of holes close to the P2/P3 interface is observed from Fig. 5e and 5f. The P1/P2 and P2/P3 interfaces exhibit sharp transitions, as indicated by abrupt changes in average BSE image intensity (cf. Fig. 5a). Holes in the film observed in P2 (Fig. 5c and 5d) show irregular projected shapes with similar size compared to Ni grains. The P1/P2 interface reveals no significant change in topography (cf. Figure 5b and 5d). The P2/P3 interface, however, exhibits large topographical contrast (see Figure 5f). In P3 the

projected size of holes is smaller than that observed in P2. Furthermore, Ni-rich grains are elongated along the direction perpendicular to the interface, indicating directional mass transport.

EDXS mapping of the interface structure displayed in Figure 6a confirms the direct correlation of bright and dark BSE image contrast with the presence (or respective absence) of Au and Ni, respectively. In P2 EDXS intensities of Ni are indistinguishable from experimental noise (Figure 6b). In P3, the Ni signal increases significantly, confirming the accumulation of Ni in this region. The elemental distribution map for Au (Figure 6c) confirms that P2 is comprised mostly of Au, while the irregular shapes in P2 are identified as holes in the annealed film. An accumulation of holes at the P2/P3 interface is confirmed by strong silicon-specific EDXS signals in Fig. 6d.

BSE micrographs in Figure 7 demonstrate the gradual change of microstructure in area P4. In the area near P3 (Figure 7a), Ni islands appear elongated along the interface normal. When approaching P5, the Ni islands become more equiaxed (Figure 7b), and reveal some faceting. The average size of Ni and Au grains near P5 is around 300 nm. The majority of holes observed in P4 are located at Au/Ni phase boundaries.

Figure 8 shows BSE and SE images of regions P5, P6 and P7 recorded by T1 and ETD detectors, respectively. In P5 (Fig 8a and 8b), Ni and Au grains have grown to approximately 400 nm. Some Au grains have accumulated and may have grown abnormally as large as 1.5 μm . In P6 (Figure 8c and 8d) the bilayer film has ruptured and became discontinuous. Remaining clusters of small Au islands are observed on the exposed substrate. In P7 (Figures 8e and 8f), the bilayer film is completely agglomerated, and individual Ni islands larger than 1 μm are observed. Small amounts of gold are visible as bright contrast at the perimeter of Ni islands in Figure 8e and 8f. The inset in Figure 8e is a false-color coded EDXS elemental distribution map recorded

from the marked area. The chemical distribution map confirms that Au decorates the perimeter of isolated Ni particles.

The complex morphology of the as-annealed metal bilayer film requires a direct comparison to single-component metal films annealed under identical conditions. Figure 9a and 9b show SEM micrographs of the annealed 30 nm single layer Ni film, which reveals a homogeneous distribution of hole formation. The single layer Au film, however, has agglomerated mostly in the center region of the substrate, while it still remained mostly continuous closer to the edge of the substrate wafer (see Figure 9c and 9d). The transition region where the film is partially ruptured is marked in Fig. 9c.

Figure 10 shows SEM images of another Au/Ni bilayer film that was annealed at 450°C. After annealing the film exhibits similar morphologies compared to the results observed at higher temperature. Consistent with Figure 1b regions with different morphologies were labeled P1' through P7'. P1' represents the largest area of the wafer with mostly homogeneous contrast under the respective imaging conditions. Relatively bright contrast and increased roughness were observed in P5', indicating the accumulation of Au. P7' is the edge of the wafer where a continuous Ni film was observed. The widths of P2' and P3' were determined from BSE micrographs and compared with the corresponding regions annealed at 675°C (cf. Table 2). For the sample annealed at 450°C, the width of the Au-rich band is approximately 300 nm, which is significantly narrower compared to a width of 10 μm observed at 675°C. No Ni-rich band was observed at 450°C.

Table 2 Width of regions P2 and P3 after annealing at 450°C and 675°C

Temperature	P2 (μm)	P3 (μm)
675°C	10	3
475°C	0.3	no apparent width

Figure 11a and 11b show cross-sectional SEM micrographs of regions P4 and P5 after annealing at 675°C. The top layer represents the carbon protective layer required during FIB preparation. Brightest contrast identifies the Au-rich phase, while dark grey intensities represent the Ni-rich phase. After annealing at 675°C, both the Ni and Au layers rearranged and mixed as a continuous layer in P4 (Fig 11a). BSE image contrast reveals that the majority of the metal/substrate interface is comprised of Au/SiO₂. Voids in the metal film are predominantly located at Au/Ni/SiO₂ triple lines. Region P5 (Fig 11b) exhibits a large Au agglomerate with roughly 1.5 μm diameter, which compares well with the plan view SEM observations shown in Figure 2c. Figure 11c and 11d represent SEM cross-sectional micrographs of regions P4' and P5' after annealing at 450°C. A 20-30 nm thick continuous Au layer is observed between Ni and the SiO₂ substrate. In contrast, the Ni layer is agglomerated, inter-dispersed with Au domains, and shows some undulations of the free surface at P4' (cf. Figure 11c). In P5', however, the Ni layer remains mostly covered by Au as a result of the long-range edge retraction (see Figure 11d).

Discussion

Localized dewetting and macroscopic edge retraction

After annealing the bilayer film reveals both localized dewetting in the center region (P1) and long-range edge retraction (P4-P7), with the respective regions separated by relatively narrow regions P2 and P3. In the center region (P1), EDXS experiments have shown that the average atomic ratios between Au and Ni remain unchanged compared to the as-deposited film. Cross-

sectional SEM imaging reveals that the thickness of the agglomerated film also remains mostly unchanged after annealing. These observations therefore suggest homogeneous agglomeration within P1, and that diffusion of both metals occurred only within P1. This “dewetting” behavior is consistent with the homogeneous agglomeration of pure Ni films (see Figure 9a and 9b). Previous cross-section characterization by transmission electron microscopy (TEM) techniques has revealed that the formation of Au/SiO₂ interface configurations is energetically preferred over Ni/SiO₂ mostly due to compressive stress in as-deposited Ni films [32]. Hole formation in P1 is initiated by void nucleation at Ni/Au/SiO₂ triple junctions.

SEM observations of regions P4 through P7 further revealed that the Au layer retracted by unusually large distances from the edge of the substrate wafer, while the underlying Ni film agglomerated locally. Such long-range edge retraction was previously reported before for single crystalline Ni films with thicknesses around 130 nm after annealing at 890°C for 20 hours [27]. Kim and co-workers, however, observed edge retraction over only 4 μm, which is orders of magnitude less than observed in this study at lower temperatures within 1 hour. Surprisingly, the observed edge retraction of the Au layer is opposite to that observed from pure Au films on SiO₂/Si substrates (cf. Figure 9). The results for the Au/Ni bilayer film, therefore, suggest that the Au/Ni interface must play a dominant role for the retraction of the Au film, while the edge of the substrate wafer has likely served as a nucleation site for film retraction.

Long-range retraction of the Au film was consistently observed for multiple substrate wafers that were either cleaved using a diamond scribe, or cut using a wire saw, hence ruling out effects from specific sample handling. Instead, the curvature of the wafer edge was observed to strongly affect film retraction. No long-range retraction was observed from concave edges of the substrate wafer (cf. Figure S1 in the supplemental online materials). For convex geometries film

retraction was observed for temperatures as low as 450°C, for which the underlying Ni film remained continuous. It is, therefore, concluded that long-range edge retraction occurs when the diffusivity of Au is large enough to reduce the energetically unfavored Au/Ni interface. The Ni film remains unchanged due to a considerably lower diffusivity [33].

Generally, polycrystalline thin films are assumed to dewet homogeneously because of local capillary driven grain boundary grooving [15]. In this study, however, film agglomeration occurs homogeneously only in the center of the substrate wafer, i.e., in region P1, while long-range edge retraction is nucleated by local defect structures with convex geometry [34], and thermodynamically driven by minimizing the Au/Ni interface energy. The reason why Au and Ni layers do not separate into isolated mono-component islands on the substrate surface is the limited diffusivity for Ni compared to Au. Regions in which different agglomeration behavior is observed are separated by a relatively sharp transition region consisting of P2 and P3. The formation of P2 and P3 is caused by partial alloying of Au and Ni, which is discussed below.

Film morphology and alloying during edge retraction

During long-range edge retraction, the bilayer films exhibit varying morphology and chemical distribution of Au and Ni along the direction normal to the retracting edge. The Au layer accumulated in regions P4 and P5, while agglomeration is observed mostly within P5. Nucleation of holes during annealing is consistently located at Ni/Au interfaces, which also reinforces the conclusion of an energetically unfavored Au/Ni interface. Cross-sectional SEM imaging (Fig 11) demonstrated that Au migrates underneath the Ni film in order to reduce the metal/SiO₂ interface energy. The latter observation is consistent with cross-sectional TEM characterization previously carried out in region P1 [35].

Between the center region (P1) and edge area (P4 and P5), relatively narrow and parallel Au-rich (P2) and Ni-rich (P3) regions were observed. The metal film thickness of the Au-rich area (P2) is similar to P1, but much thinner than the Ni-rich area (P3). The intensity in Ni EDXS maps (Figures 3 and 6) show an abrupt P2/P3 interface with accumulation of holes. Furthermore, Ni grains in P3 are elongated in the direction of the interface normal. These observations suggest the diffusion of Ni away from P2 to P3. Annealing at 450°C and 675°C has revealed that the widths of regions P2 and P3 are temperature dependent (see Table 2). The accumulation of Au in regions P4 and P5 creates a relatively large chemical potential [36] for Ni at elevated temperatures, thus driving Ni diffusion from P2 towards P3 and P4. As the annealing temperature increases, the width of P2 and P3 increases due to both enhanced diffusivity and solubility between Ni and Au. The separation of Ni and Au between P2 and P3 was triggered by increased amounts of Au due to edge retraction. A more detailed kinetic study is required to unambiguously determine the formation mechanisms for P2 and P3. *In-situ* SEM annealing experiments are ideally suited for such investigations, but are beyond the scope of this report.

Figure 12 shows SEM micrographs and corresponding EDXS maps of frequently observed morphologies within the center of the substrate wafer, i.e., area P1. Similar to the observations described above, coupled Au-rich and Ni-rich concentric bands were observed. The width of the Au-rich band is roughly 10 μm , while the average width of the Ni-rich band is roughly 1.5 μm . Relatively large holes were observed within the Au rich bands and accumulation of holes occurred at the interface between Au- and Ni-rich bands. Similar to region P3, Ni grains are elongated in the radial direction indicating the direction of diffusion towards the center, where Ni is accumulated (cf. Figure 12c). This qualitative observation of concentric separation of Au and

Ni within area P1 is analogous to the previous observations of areas P1 through P3, which is triggered by heterogeneous nucleation of film agglomeration initiated by local defects in the substrate surface.

A schematic drawing summarizing the experimental observations is shown in Figure 13. Relative concentrations for Au and Ni are sketched combined with illustrations of plan view film morphologies as a function of relative distance to the edge of the substrate wafer. Figure 13a shows the as-deposited film before annealing, with the concentration of Au and Ni constant across the wafer. The top view shows only Au due to the deposition sequence. As the temperature increases, the Au film begins to retract from the edge of the wafer and accumulates in regions P4 and P5. The increased amount of Au causes undulation of the film surface and triggers local morphology transition in P4 and P5 (Figure 13b). The associated changes in chemical potential also drive the diffusion of Ni away from center towards the edge, forming Au and Ni rich bands in regions P2 and P3, respectively (cf. Figure 13c).

Conclusion

Characterization of solid state dewetting of Au/Ni bilayer films from SiO₂/Si substrates revealed both homogeneous localized dewetting and long-range edge retraction. While the Au layer was found to retract over a large distance from the edge of the wafer towards its center, Ni dewetted homogeneously across the substrate through the formation of local holes and adjacent Ni islands. Annealing of as-deposited films at different temperatures has demonstrated that long-range edge retraction occurs when the diffusivity of Au is sufficient to minimize the total Au/Ni interface energy. This mechanism is kinetically enabled at relatively low temperatures of 450°C since the Ni film remains unchanged due to lower diffusivity compared to Au. As a result

of long-range edge retraction, the bilayer film exhibits varying morphology and chemical distribution of Au and Ni over hundreds of micrometers along the direction normal to the retracting edge. The accumulation of Au causes undulation of the free surface and triggers the local morphology transition. The associated change in chemical potential causes diffusion of Ni, thus forming Au and Ni rich bands. Overall, this study demonstrates that local morphological changes and long-range edge retraction coexist during the dewetting process of metal bilayer films. Different self-diffusivities for the metal components, interface between two metal layers, and alloying have a critical effect on the dewetting process of bilayer films.

Acknowledgements

This study was financially supported by a Faculty Early Career award from the US National Science Foundation (DMR-0955638). X.Z. was supported by UC Laboratory Fee grant #12-LR-238313. Assistance with magnetron sputtering of Ni films by Drs. Greene and Kai Liu was invaluable. We acknowledge Mr. Wei Qin for help during cross-sectional SEM imaging. The FEI Scios dual-beam instrument utilized in this study is located at the Center for Nano and Micro Manufacturing at UC Davis and was funded through a DURIP award from the Office of Naval Research under grant number #N00014-13-1-0668 (program manager: Dr. Lawrence Kabacoff).

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Figure Captions:

Figure 1: (a) A schematic of the as-deposited bilayer film. (b) Plain-view optical micrograph of the sample after annealing. (c) SEM micrograph of the surface area marked in (b). (d) SEM micrograph of the surface area marked in (c). SEM micrographs taken by the ETD detector show varying morphologies labeled from P1 to P7.

Figure 2: (a) Cross-sectional SEM micrograph of the annealed sample taken by the ETD detector. (b-d) SEM micrographs of the annealed sample surface at different areas taken by the BSE (T1) detector. (b) the area from P1 to P4. (c) the area from P4 to P6. (d) the area from P6 through P7.

Figure 3: EDXS chemical distribution maps and corresponding SEM survey image. (a) is the SEM survey micrograph. (b), (c) and (d) are EDXS chemical distribution maps obtained from spectral intensities of the Ni $L\alpha_{1,2}$ (red), Au $M\alpha_1$ (yellow) and Si $K\alpha_1$ (blue). Vertically integrated spectral intensities for each element are also plotted as a function of relative distance in (a).

Figure 4: SEM micrographs of the annealed sample surface in region P1 taken by BSE T1 detector (a) and in-column T3 detector (b), respectively.

Figure 5: (a) and (b): SEM micrographs of areas P1 through P3 captured by T1 and ETD detector, respectively. (c) and (d): SEM micrographs of the interface P1/P2 taken by T1 and ETD detector, respectively. (e) and (f): SEM micrographs of the interface P2/P3 taken by T1 and ETD detector, respectively.

Figure 6: EDXS chemical distribution maps and corresponding SEM survey image of the areas from P1 through P3. (a) is the SEM survey micrograph. (b), (c) and (d) are EDXS

chemical distribution maps obtained from spectral intensities of the Ni L α 1_2 (red), Au M α 1 (yellow) and Si K α 1 (blue), respectively.

Figure 7: BSE micrographs showing the gradual change of microstructures in area P4. (a) is the BSE image of the area near P3. (b) is the BSE image of the area approaching P5.

Figure 8: SEM micrographs of the areas P5 through P7 captured by the T1 (a, c, e) and the ETD (b, d, f) detector respectively. (a) and (b) show the surface of region P5. (c) and (d) show the region P6. (e) and (f) show the region P7. The inset of (e) is the EDXS elemental map recorded in the marked area used to identify chemical composition of microstructural features.

Figure 9: (a) and (b): SEM micrographs of the annealed 30 nm Ni single layer film at low (a) and high (b) magnification, respectively. (c) and (d): SEM micrographs of the annealed 30 nm Au single layer film at low (c) and high (d) magnification, respectively.

Figure 10: SEM micrographs of the 450°C annealed sample surface taken by BSE T1 detector (a) and ETD detector (b), respectively. **Brightness and contrast of the presented micrographs were adjusted for better presentation.**

Figure 11: (a) and (b): Cross-sectional SEM micrographs of P4 (a) and P5 (b) after annealing at 675°C. (c) and (d): Cross-sectional SEM micrographs of P4' (c) and P5' (d) after annealing at 450°C

Figure 12: EDXS chemical distribution maps and corresponding SEM survey images of the concentric opposite diffusion phenomena in the center area. (a) and (b) are the SEM survey micrographs taken by the ETD detector (a) and the T1 detector (b), respectively. (c), (d) and (e) are EDXS chemical distribution maps obtained from spectral

intensities of the Ni $L\alpha_{1_2}$ (red), Au $M\alpha_1$ (yellow) and Si $K\alpha_1$ (blue). Brightness and contrast of the presented micrographs were adjusted for better presentation.

Figure 13: A schematic of edge retraction and opposite diffusion behavior in bilayer film during annealing. The top two curves of each sketch are relative concentration of Au and Ni as a function of relative distance. The bottom represents the plain view of the sample surface during the process: (a) as-deposited bilayer film. (b) shows partial Au retraction and opposite diffusion behavior of Au and Ni. (c) demonstrates the formation of coupled Au-rich and Ni-rich areas.

Figure 1

Figure 2

Figure 3

Figure 4

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