

Alloy Destabilization Behavior of Cu-Ni Thin Films on Si during Solid State Dewetting

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Abstract:

Synthesis of nanoparticles research witnessed a remarkable headway with techniques spanning a wide range of materials and offering good control over particle shape and size. Top-down approaches have become successful in achieving controlled positioning of nanoparticles in pre-defined templates. A self-assembly method, however, is highly desirable because of its simplicity and compatibility with heterogeneous integration processes. Thin elemental or multicomponent films can be destabilized into self assembled arrays of nanoparticles. We will discuss how heating of ultrathin films can be a powerful but simple tool to fabricate functional nanostructures. Thin metal films on inert substrates are generally unstable, with their free energy resembling that of a spinodal system. Such films can spontaneously evolve into predictable morphologies with defined length scales. This process has been extensively used to prepare arrays of catalyst nanoparticles on Si surfaces for growth of vertically aligned carbon nanofibers. In this work we report on the behavior of Cu-Ni alloy thin films during solid state dewetting. The segregation of Cu-Ni alloy thin films during solid state destabilization on Si is in contrast to behavior expected from isomorphous system. Thin films of Cu-Ni and Ti-Cu-Ni were formed on Si and subjected to annealing temperatures from 300 °C - 700°C. The resulting particles formed by both dewetting and reaction with the substrate were distinguished by selective wet etching and characterized by scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDX).

Introduction:

Dewetting of thin, metastable, adjoining films into arrays of nano particles on solid substrates is important not only due to complexities of the basic interactions involved in wetting phenomena but also due to its technological importance.^{1,2} Metal thin films deposited by physical vapor deposition could be sent to a metastable state due to the low mobility of atoms. When heated, the film/substrate system changes caused due to reduction in the total energy of the system with respect to the initial energies of the surfaces of the film/ambient and film/ substrate and the resulting particles. Liquid- and solid-states, dewetting regimes have been distinguished corresponding to fluidic or diffusive type of mass transport.^{3,4} Liquid phase dewetting has been widely studied in various model systems such as polymer films and metals under pulsed laser irradiation.⁵ Solid-state dewetting has been observed to occur at temperatures below the melting temperature of the film via atomic diffusion.^{4,6} For liquid state dewetting this process is initiated by hole nucleation and growth into a connected network of

rivulets and finally formation of disconnected nanoparticles with a characteristic “cellular” arrangement, i.e., chains of nanoparticles dividing large nanoparticle-free regions.² In realistic and technologically important systems there can be a strong exchange of material between the film and the substrate. In the case of nickel films on silicon the formation of silicides has been extensively reported.^{7–12} The dewetting system in which there is a considerable mass transport across the film-substrate interface is termed reactive dewetting.¹³ The dewetted structure that is formed during reactive solid-state dewetting depends on the relative rates of film dewetting, chemical reaction with the substrate, and wetting or dewetting of the film on the reaction products. In this paper we present observations of solid-state dewetting of thin films of Cu-Ni were formed on Si and subjected to annealing temperatures from 300 °C - 700°C for 4 h. The resulting particles formed by both dewetting and reaction with the substrate were distinguished by selective wet etching and characterized by scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDX).

The substrates used in the experiments were (100) Si 100 mm diameter As-doped wafers. Cu–Ni alloy deposition was performed by simultaneous evaporation of Cu and Ni at pressures below 10^{-6} Torr. Cu to Ni ratio was controlled by adjusting the deposition rates to 0.9 Å/s for copper and 0.3 Å/s for nickel monitored by crystal oscillator. The deposition was terminated at thicknesses of approximately 37.5 nm of Cu and 12.5 nm of Ni using manual shutters. These wafers were then diced into 1X2 cm² chips. Individual chips were annealed at 300, 400, 500, 600, and 700 °C at a ramp rate of 20 °C/min inside a steel tube. The heating was done at a rate of approximately 20 °C/min while flowing a 1% H₂ by volume in N₂ balance forming gas mixture at approximately 3 ml/s. The target temperature was held constant for 4 h and then lowered at a rate ranging from 45±15 min for 300–400 °C and 2±1 h for 500–700 °C. Samples were removed from the furnace below 100 °C.

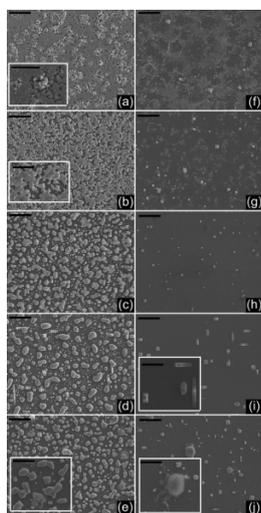
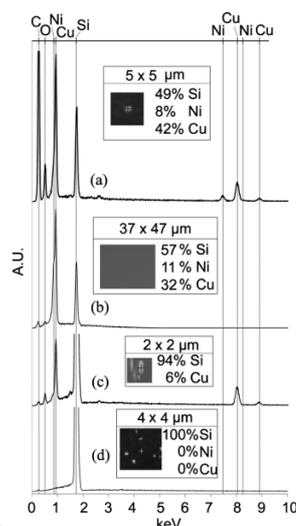


FIG. 1. SEM images of 50 nm 75Cu–25Ni (vol %) alloy films annealed between 300 and 700 °C and of samples annealed under identical conditions but also etched with Kallings reagent No. 2. Insets (a) and (f), (b) and (g), (c) and (h), (d) and (i), and (e) and (j) were annealed at 300, 400, 500, 600, and 700 °C, respectively. Insets (a)–(e) are of samples after annealing. While (g)–(j) are of samples annealed under identical conditions as those shown in (a)–(e) with an additional etch using Kallings reagent No. 2. Scale



bars are 2 μm long for the panels and 1 μm long for the insets.

FIG. 2. EDX spectra after annealing the 50 nm 75Cu–25Ni (vol %) films of (a) a particle grown at 700 °C and removed from the substrate and examined on carbon tape spectrum, (b) is of the as-deposited film taken with a 5 kV acceleration voltage, (c) is of a particle formed at 600 °C, and (d) is from the area of the substrate between particles after a 600 °C anneal and Kallings reagent No. 2 etch. Compositions are reported in at. %. Insets designate the location of the point probe or for (b) the scan area that produced the signal

The variation in progression of dewetting at temperatures from 300 to 700 °C with a 4 h anneal is presented in Fig. 1. Annealing to 300 °C resulted in only branched elongated holes that appear to nucleate along the grain boundaries. The hole shapes and patterns shown in Fig. 1 indicate that solid-state dewetting takes a distinctly different path compared to that of liquid phase dewetting. In liquid films, dewetting begins with the formation of typically larger, circular holes for a film of similar thickness to these studied here.^{5, 15} The irregular holes in the film grow and merge without the presence of any cellular structure, as temperature is increased (Figs. 1(b) and 1(c)). As the holes grow along the film's grain boundaries, the film becomes a discontinuous set of faceted, polydispersed particles (Figs. 1(c) and 1(d)).

After annealing, light features surrounding or surrounded by a dark background were visible in SEM (left side of Fig. 1). The dark background was identified as exposed Si substrate with a small amount of detected copper and nickel after EDX compositional analysis of a sample annealed at 700 °C reported a composition of 95%–100% by weight silicon with trace amounts (1%) of copper and nickel. EDX analysis of lighter regions showed high copper, nickel with substantial variations in relative Cu/Ni ratio from region to region. This is an unexpected result since the assumption was that $\text{Cu}_x\text{Ni}_{1-x}$ is an isomorphous system and segregation would be improbable. A 10 min wet etch with Kallings reagent No. 2 completely removed the as-deposited copper nickel alloy. SEM of annealed samples after wet etch showed that most of the dewetted film material was removed except for mostly rectangular faceted particles (right side of Fig. 1). Their resistance to chemical etch indicates the change in bonding (metal to covalent), suggesting that these particles are silicides in nature. Elemental presence was determined by EDX with a Hitachi S-3200N SEM at 5, 15, and 20 kV. Particles were examined for silicon content against carbon tape and relative silicon to nickel to copper content was seen to vary. The spectrum and composition of one

with mixed copper and nickel character are shown in Fig. 2(a). EDX of the as-deposited film reveals silicon, copper, nickel, and carbon peaks with an almost 3:1 atomic ratio between copper and nickel (Fig. 2(b)). Compositional analysis of a particle on silicon substrate present after 700 °C anneal and CuNi alloy etch removal is shown in Fig. 2(c). EDX of the substrate area between particles after annealing at 600 °C and etch removal of Cu-Ni alloy showed that this area contained silicon (Fig. 2(d)). Substrate area exposed by a receded film after annealing at each temperature was determined by image analysis of three SEM images of each sample.¹⁶ The extent of dewetting is indicated by the percentage of exposed substrate area, which increases with temperature up to approximately 600 °C. The extents of dewetting for each temperature after 4 h are 8.98% at 300 °C, 23.1% at 400 °C, 50.3% at 500 °C, 63.3% at 600 °C, and 60.4% at 700 °C. From 600 to 700 °C the unexpected 2.9% drop in the extent of dewetting is attributed to a 3.2% increase in silicide particle coverage.

A second type of a feature that can be readily distinguished in Fig. 1(a) is a protrusion that elevates the film off the substrate. The nature of these protrusions was elucidated by removing the Cu–Ni alloy by etching with Kalling’s reagent No. 2 for 10 min, thus exposing the substrate and particles not removed by the etchant (Figs. 1(f)1(j)). Characteristics that determined what particles were used in size and number density calculations included etch resistance, a rectangular shape as seen from a top down view of the (100) silicon surface, and alignment of boundaries along Si (011) and (0-11) directions. Alignment of Ni and Cu silicide particle edges along the (011) and (1-10) directions has been previously reported for Ni and Cu silicides.^{8,14} For 300, 400, 500, 600, and 700 annealing temperatures, substrate areas covered by particles are 0.54%, 1.47%, 1.83%, 2.57%, and 5.63%, respectively. The average numbers of particles formed for an 11.6X9.3 μm^2 area for 300, 400, 500, 600, and 700 °C are 7.5, 46, 61, 21, and 98 particles, respectively. The sizes or average areas per particle are calculated for 300, 400, 500, 600, and 700 °C as 7.82×10^{-2} , 3.52×10^{-2} , 3.22×10^{-2} , 1.31×10^{-1} , and 6.3×10^{-2} μm^2 , respectively.¹⁶ The number of particles formed generally increases with temperature, except for samples processed at 600 °C where significantly fewer particles with significantly larger average size are present. In order to characterize the samples below the substrate level silicon was etched with KOH. The resultant structure for the 700 °C sample is shown in Fig. 3(a). In the center of the mounds, denoted by arrows in Fig. 3(a), is either an aligned silicide particle or a particle with lighter edges that are not aligned. Surrounding these particles are areas that vary in thickness and are lighter than the silicon substrate possibly indicating copper or nickel doping. The number of these features visible after etch is 657, similar to the number of dewetted particles, 730, for a given area of three 11.6 X 9.3 μm^2 images. The features that shows etch resistance to KOH silicon etch are concluded to be related to the number of dewetted particles at this temperature. The observations described here present us with the following model of the simultaneous processes (Fig. 4). Interdiffusion for Cu and Ni into Si substrate and Si from the substrate into Cu–Ni film reduces the interfacial energy and eventually locks the Cu–Ni islands into an irregular shape. Redistribution of the film on the surface due to dewetting leads to nonuniform doping of the substrate with a pattern corresponding to the pattern of the dewetted film accompanied by growth of silicide crystals spanning across the substrate–film interface.

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