Role of silver nanoparticles in the dewetting behavior of copper thin films

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ABSTRACT

We report on the effect of added silver on the solid state dewetting behavior of copper thin films, grown by thermal evaporation. The films were annealed under different conditions, conventional furnace annealing in air and argon and rapid thermal annealing in nitrogen. Our results show that for all annealing conditions, addition of silver to copper films suppresses the dewetting when compared to pure copper films. Fully dewet silver—copper films produce roughly spherical nanoparticles, with the amount of silver controlling the particle areal density and size distribution. This provides an additional parameter for controlled synthesis of nanoparticles by a bottom–up approach.

1. Introduction

Metallic films are widely used as interconnects in electronic devices. The high temperature performance of these devices is limited due to failure of the interconnects, because the films are metastable in the as-deposited state [1]. Annealing causes the continuous film to rupture and break down into individual aggregates. This process, driven by the minimization of the total energy of all surfaces and interfaces in the system, is called dewetting [2]. The dewetting rate increases with decreasing film thickness and increasing annealing temperature [3]. While the process is generally considered to be detrimental, dewetting can also be harnessed as a technique for fabrication of metallic [4–7], semiconductor [8,9], and alloy [10,11] nanoparticles, which have wide applications in the fields of plasmonics, magnetic recording medium, medicines, and catalysis [11–15].

The thermal destabilization of thin films can take place by two different mechanisms, liquid and solid state dewetting. The mechanism depends on whether the film locally melts or dewetting occurs when the film is still in the solid state. In liquid state dewetting, films are annealed above the melting temperature and instability is governed by the hydrodynamic flow of liquid metal [16,17]. In solid state dewetting, films are annealed below the melting temperature and dewetting is governed by the formation of holes at the grain boundaries followed by edge retraction leading to interconnected ligaments. These ligaments finally form particles via a surface diffusion mediated process [3]. Solid state dewetting is also considered as a bottom–up technique to fabricate nanoparticles [18]. It can be integrated with photolithography to create ordered arrays of metallic nanoparticles [19].

In the solid state, dewetting initiates at pre-existing voids or by the nucleation of new voids via thermal grooving at the grain boundaries, triple junctions, and/or film-substrate interface [20]. Kwon et al. studied the agglomeration behavior of sputtered Au and Cu films on silicon dioxide, where they observed that the films agglomerate through grain boundary grooving and the final island size depended on the temperature [21]. The effect of annealing atmosphere on the dewetting of thin Au films was also investigated, where it was observed that annealing in air resulted in smaller grains compared to annealing in forming gas. This was attributed to the higher surface energy anisotropy in the films when annealed in forming gas [22].

There have been several reports on dewetting of bilayer films and subsequent formation of alloy nanoparticles. These have focused on systems, where material is deposited in the form of bilayers or multilayers. Amram et al. observed that Au–Fe bilayer thin films had a higher thermal stability than pure Au films because of the low density of defects in a single crystalline film, which reduced the formation of holes [23]. Similarly, the addition of Pt to Au thin films delayed the thermal agglomeration process, which was attributed to the effect of Pt on the grain size [24]. The stacking sequence of bilayer films also influenced the mechanism of solid state dewetting, as demonstrated in the W–Au system, where the elements are immiscible and have different crystal structures. W acted as a passivation layer for dewetting of Au film and changed the wettability of Au [25]. Ag capping layers, on FePt films, increased the in-plane tensile stress, improved (001) anisotropy, and $L1_0$ ordering of the layers, which prevented dewetting during rapid thermal annealing of the films [26]. Thus, existing reports on single crystal and/or oriented polycrystalline bilayer or multilayer films indicate that the addition of a second layer of material increased the overall film stability. In this work, we focus on the addition of a second

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layer, which forms nanoparticles in the as-deposited state and is immiscible with the thin film. We study the role of these nanoparticles on dewetting of the film, under different annealing conditions.

We study the dewetting in the copper–silver system, primarily the effect of silver deposition and annealing atmosphere on the thermal stability of polycrystalline copper films. Cu and Ag crystallize in the fcc structure, with limited solid solubility. The lattice parameters are 0.36 and 0.41 nm for Cu and Ag respectively. This is a 13% atomic size difference, which results in a positive enthalpy of mixing in the solid state [27]. Deposition of silver on polycrystalline copper films leads to the formation of nanoparticles. We report on the effect of annealing conditions and addition of silver on the dewetting behavior of copper films. Further, using rapid thermal annealing, we also fabricated pure Cu nanoparticles and Cu–Ag nanoparticles, with the silver controlling the sizes and areal densities of the formed nanoparticles.

2. Experimental details

The starting substrates used were p-type Si (100) wafers, purchased from Semiconductor Wafer, Inc. The as-received wafers were cleaned using trichloroethylene, acetone, nitric acid, hydrofluoric acid, and deionized water and dried using a nitrogen blower. Since Cu reacts with Si, an oxide layer (~100 nm thick) was grown by dry oxidation at 1200 °C for 2 h using a Tempress Systems furnace. The oxide layer thickness was measured using an ellipsometer, J.A. Woollam Co. Inc., M–2000VI.

The Cu and Ag were deposited in a thermal evaporation chamber, HPVT 303, supplied by Hydro Pneo Vac Technologies. The chamber reaches a base pressure of 2×10^{-6} mbar and it is possible to deposit up to three metals, without breaking vacuum. The wafers were placed in a substrate holder and then loaded in the evaporation chamber. The copper film was deposited from 99.99% pure pellets procured from Sigma Aldrich. After copper deposition, silver was thermally evaporated from a 99.99% pure source procured from Alfa Aesar. The deposition rates for copper and silver were maintained at 0.03 and 0.02 nm/s respectively and were controlled using a quartz crystal oscillator based thickness monitor. The films were also deposited on amorphous carbon (a-C) grids, which were placed contiguously with the oxidized Si wafers. These grids were used for imaging the as-deposited films. All depositions were carried out with the substrates held at room temperature.

The deposited films were then annealed ex-situ under different atmospheres and annealing conditions. The films were annealed in a conventional muffle furnace in air and argon atmosphere and in a rapid thermal annealing (RTA) system, AnnealSysAS-One 100, under nitrogen atmosphere. The annealed samples were characterized by scanning electron microscopy (SEM), Inspect F, FEI operating at an accelerating voltage of 20 kV. The films on the a-C grid were characterized using transmission electron microscopy (TEM), Technai F20, operating at 200 kV. The hole/particle size, density, and exposed substrate area fraction were analyzed using Image J and HLImage software packages.

3. Results and discussion

The bright field TEM image of the as-deposited, 20 nm thick, copper film on a-C grid is shown in Fig. 1(a). The film is polycrystalline in nature and the grain size was calculated using HLImage. The obtained size distribution is shown in Fig. 1(b) and the average size and standard deviation was calculated to be 10.6 ± 7.5 nm. This is consistent with normal grain growth in evaporated metallic films [28]. Ag was then deposited on 20 nm Cu, in the same chamber, without breaking vacuum. Surface energy of Ag (1210 mJ m^{-2}) is lower than that of Cu (2130 mJ m^{-2}) [29] and hence, silver should grow on copper as two dimensional layers. Because of the polycrystalline nature of the Cu and the frustrated diffusion during deposition at room temperature, the

deposited silver tends to form islands. Fig. 2 is a representative TEM image of the Ag deposition on Cu. The particle formation is random and some formed particles show Moiré fringes due to the lattice mismatch between the two metals. Similar fringes have been observed in other systems, such as Au–Bi [30]. These depositions (pure Cu and Ag–Cu) were also carried out on oxidized Si substrates (along with the TEM grids) and the films were annealed ex-situ under different conditions.

When the Cu and Cu–Ag films were annealed at 700 °C for 4 h in air, dewetting was initiated. This can be seen from representative SEM images in Fig. 3, where the formation of pinholes is seen. The pinholes can be more clearly seen in the case of pure film (Fig. 3(a)) and when Ag is added, their formation is suppressed and their areal density and size decreased with increasing Ag addition. It has been reported that Cu films sputter deposited on silica completely dewet when heated at 700 °C for 15 min in a reducing atmosphere [21], while in air we only observe individual pinholes even after 4 h of annealing. This difference can be attributed to the formation of copper oxide. There have been several observations on the formation of copper oxide when annealing in air [31–38]. The formation of copper oxide complicates the dewetting process since oxidation competes with dewetting and restricts void nucleation via grain boundary grooving, resulting in smaller pinholes compared to annealing in an inert atmosphere [39]. When Ag is added, it further retards the dewetting of the films, as seen from Fig. 3(b) and (c). Hence, when the film is heated in air we should consider the competition between oxidation and dewetting in a Cu film with added Ag nanoparticles. The amount of Ag added is not sufficient to suppress Cu oxidation. However, because the Ag nanoparticles are randomly distributed on the surface, with some of them found at grain boundaries and triple junctions, it is likely that the silver suppresses the void formation at these locations. To verify the effect of atmosphere, we annealed pure Cu and Cu–Ag films in argon and nitrogen. The aim is to suppress oxidation and study the effect of Ag on the film dewetting.

In Argon atmosphere, annealing was carried out at 600 °C for 2 h, at a lower temperature and for a shorter duration than in air. The film morphology is drastically different, with clear formation of pinholes and agglomerates, as seen in Fig. 4. Addition of Ag to these films reduces the size of the formed pinholes, with the decrease directly proportional to the amount added. A similar behavior was observed in air, where the silver suppressed the dewetting of oxidized copper film. While a direct comparison of the two situations cannot be carried out, since in air, dewetting is in competition with oxidation, it is important to note that in both cases silver reduces the pinhole size and areal density.

The morphologies of the films annealed in the RTA system, at an even lower temperature of 400 °C and hold time of 5 min, are shown in Fig. 5. These are similar to those obtained in Fig. 4. Once again, the addition of silver, in the starting polycrystalline Cu film, suppresses the pinhole size. To quantify this effect, pinhole sizes were measured from the SEM images, for different annealing conditions, and the data is summarized in Table 1. It can be seen clearly that for each annealing atmosphere (air, argon, or nitrogen) the addition of Ag reduces the pinhole size. In air, the pinhole formation is influenced by the competition between dewetting and oxidation and the sizes obtained cannot be directly compared to the other two atmospheres. Pinhole sizes are similar for Ar and N_2, with their size in the case of RTA annealing being slightly smaller.

Annealing of polycrystalline thin films leads to grain growth via two modes, normal or abnormal growth mode. Normal grain growth is observed at early states of film growth where the grain size is comparable to the thickness [40], while abnormal growth refers to the preferential growth of low energy grains at the expense of other grains. In our system (pure Cu and Cu–Ag), we do not observe any abnormal grain growth during annealing. With further rise in temperature, dewetting is initiated in the film with the formation of pinholes at boundaries and other defect sites. These pinholes grow and as they meet, an interconnected structure is obtained. With further increase in