Microsc. Microanal. 21 (Suppl 3), 2015
doi:10.1017/S1431927615004675 Paper No. 0388

Wetting and dewetting of ultra-thin Ni films on Si and SiO_2 substrates

Klaus van Benthem

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

Wetting of thin films on substrates and their solid state dewetting behavior at elevated temperatures is governed by the balance between free surface energies of film and substrate, and the respective interface energy. For many materials system, including Ni on silicon, solid-state reactions at the film substrate, defect segregation, and interfacial stress can cause interdiffusion across the interface plane and alter the wetting behavior [1]. For polycrystalline films dewetting is often initiated by grain boundary grooving at locations where grain boundaries intersect the free surface of the thin film.

Aberration-corrected scanning transmission electron microscopy (STEM) combined with electron energy-loss spectroscopy is an ideal tool to characterize the cross-sectional interface structure and local bonding configurations, respectively. In situ transmission electron microscopy (TEM) further allows monitoring of changes in film morphology and interface structure as a function of temperature and time. However, the self-diffusion length of Ni at 864 K and 1296 K is 0.04 nm and 25 nm within 1s, respectively. Hence, dynamic transmission electron microscopy (DTEM) is required to evaluate dewetting behavior for homologous temperatures above 0.5.

In this presentation recent results obtained for thin polycrystalline Ni films on both Si and SiO_2 substrates will be reported. Thin films of Ni with nominal thicknesses ranging between 5 and 30 nm were deposited at room temperature by DC magnetron sputtering. When Ni is co-deposited with Pt on clean Si substrate surfaces, the formation of a pre-silicide layer below $Ni_{1-x}Pt_xSi$ films was observed with structure and composition distinctly different from previously observed diffusion layers [2]. It was found that during two-step rapid thermal annealing Ni interstitial diffusion can kinetically dominate over the formation of Ni silicide, which results in a metastable pre-silicide layer (Figure 1). The pre-silicide layer was found to limit diffusion of Ni into the Si substrate and, therefore, allows for the low-temperature growth of Ni_2Si and NiSi [2].

Alternatively, when Ni is deposited on thermally grown amorphous SiO_2 no interdiffusion between film and substrate takes place. *In situ* heating experiments revealed formation of holes within the metal film that nucleate at the Ni/SiO_2 interface rather than at the free surface of the film. Ni islands were observed to retract, in attempt to reach equilibrium on the SiO_2 layer. The formation of graphene layers between the metal film and the SiO_2 substrate was observed during film agglomeration, which indicates lowering of the Ni/SiO_2 interface energy (Figure 2). Cr, which is considered an impurity in this study, forms surface oxide layers on the free surface of SiO_2 and the Ni islands. Cr does not prevent dewetting of Ni at elevated temperatures, but will likely have altered the equilibrium shape of the Ni islands [3].

The kinetics for the dewetting of Ni films from SiO_2/Si substrates can be evaluated through DTEM. Initial experiments with laser energies leading to temperatures close to the melting point of Ni reveal metal drop formation on the substrate surface with morphologies typical for spinodal decomposition. In thin parts of the TEM sample metal droplets are ejected form the substrate surface, while interfacial stresses due to the misfit

in thermal expansion coefficients between film and substrate cause fracturing of the silicon substrate [4].

References

[1] Thron AM, Greene P, Liu K, van Benthem K. Structural changes during the reaction of Ni thin films with (100) silicon substrates. Acta Mater 2012;60:2668–78.
[2] Thron AM, Pennycook TJ, Chan J, Luo W, Jain A, Riley D, et al. Formation of pre-silicide layers below $Ni_{1-x}Pt_xSi/Si$ interfaces. Acta Mater 2013;61:2481–8.
[3] Thron AM, Greene P, Liu K, van Benthem K. In-situ observation of equilibrium transitions in Ni films; agglomeration and impurity effects. Ultramicroscopy 2014;137:55–65.
[4] Hihath S, van Benthem K et al., in preparation (2015)
[5] This work was supported by a CAREER award of the US National Science Foundation (DMR-0955638), and a UC Laboratory Fee grant (#12-LR-238313).

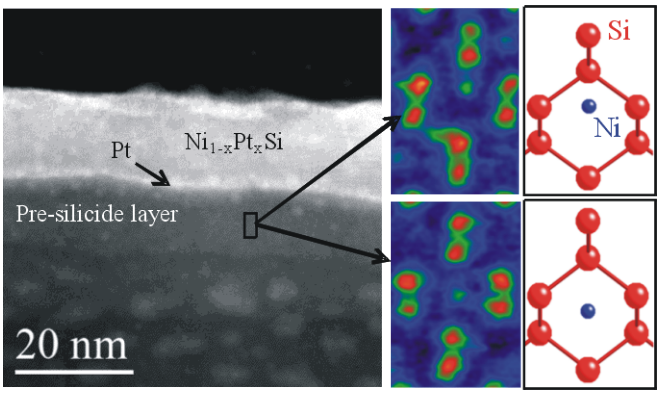

Fig. 1: Annular dark field STEM image of the Ni(Pt)Si layer deposited on the Si substrate. Underneath the silicide film the pre-silicide layers is observed that reveals Ni in different interstitial configurations. Reproduced with permission [2].

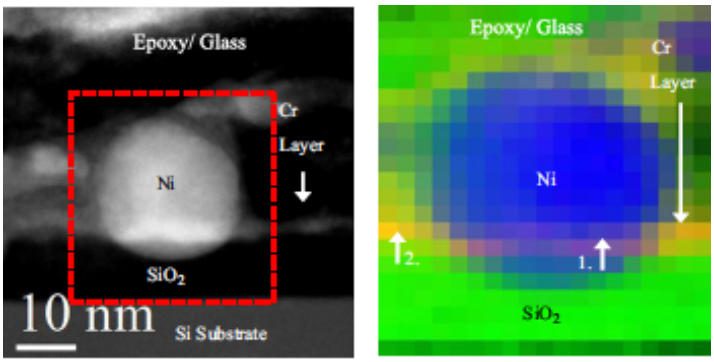

Fig. 2: High-angle annular dark field STEM image (left) of a Ni island supported by a roughly 10nm thick thermal SiO_2 film. The right image shows the corresponding spectrum image with blue color representing Ni, red representing Cr, and green representing O. Reproduced with permission [3].