Scripta Materialia xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Scripta Materialia

journal homepage: www.elsevier.com/locate/scriptamat

Mechano-stimulated equilibration of gold nanoparticles on sapphire

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ARTICLE INFO

Article history:
Received 14 May 2015
Revised 3 June 2015
Accepted 4 June 2015
Available online xxxx

Keywords:
Interfaces
Surface energy
AFM
Nanoindentation
Surface diffusion

ABSTRACT

We present a new method for equilibration of faceted nanoparticles obtained by solid state agglomeration (dewetting) of metal thin films. The method relies on crystalline defects introduced in the particles by the atomic force microscopy-based indentation and tapping. The developed method was employed for statistically based determination of the Au {1 1 1}/sapphire {0 0 0 1} interfacial energy, with the result (2.11 ± 0.08 J/m^2) being in good agreement with the values reported in the literature.

Experimental determination of the relative interface and surface energies of small anisotropic crystals is based on the Wulff analysis [1] for the free-standing crystals, and on the Kaischew–Wulff–Winterbottom analysis [2,3] for the crystals grown on foreign substrates. Small crystalline metal particles on substrates can be produced by annealing thin metal films deposited on non-wetting substrates either above or below the melting point of the metal. The latter method is known as a solid state dewetting [4–6]. In conjunction with transmission electron microscopy (TEM), it was employed already in late 1960s for the analysis of the metal particles on ceramic substrates [7]. In more recent works, focused ion beam (FIB) 3D tomography combined with TEM was employed for precise reconstruction of equilibrium crystal shape (ECS) of gold on sapphire [8] and platinum on ZrO_2 and Si_3N_4 substrates [9], and determining the respective metal–ceramic interface energies. Both TEM and FIB methods allow direct measurement of the distance between the center of the equilibrated single crystalline particle on a substrate and the individual interface/facets, and determining the relative interface/surface energies employing the relationship derived by Kaischew [2–3]:

$$\frac{R_t}{R_s} = \frac{\gamma_{sp} - \gamma_{pv}}{\gamma_{sv}} \quad (1)$$

where R_t, R_s is the distance from the particle center to the facet and to the substrate, respectively, and γ_{sp}, γ_{pv}, γ_{sv} are the energies of the particle/substrate interface, of the facet, and of the substrate surface, respectively.

The main drawback of the TEM and FIB-based methods, as pointed out in Ref. [10], is labor- and time-consuming sample preparation, which limits the statistical sampling size of the acquired data. Moreover, it is unclear whether the individual particles selected for analysis have reached the state of thermodynamic equilibrium. Additional limitation of the above methods is the requirement for the center of the Wulff shape to be located in the particle (i.e. above the substrate), so that it can be determined from the cross-sectional particle's image. In some cases, however, the center of the Wulff shape lies below the substrate (when $\gamma_{sp} < \gamma_{sv}$), and the geometry of the particle cannot be used for finding this central point. Thus the number of material systems that can be studied using these TEM and FIB-based methods is limited. Statistical techniques for studying the nanoparticles obtained from ultra-thin films include grazing incidence small angle X-ray scattering [11], and scanning tunneling microscopy [12], which allow determining the aspect ratio of the particles. These methods are technically complicated and have limitations with respect to the maximum particle size. This is why there are very few works in the literature in which the solid–solid interface energy is determined employing the Kaischew–Wulff–Winterbottom analysis of the equilibrium shape of small crystals on substrates. Müller and Spolenak proposed an alternative approach to determining interface energies based on atomic force microscopy (AFM) measurements of aspect ratio of a large number of submicrometer-sized particles on a substrate [10]. The average energy values obtained in their work agreed well with the values obtained with the aid of the 3D FIB tomography method, though the authors admitted

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http://dx.doi.org/10.1016/j.scriptamat.2015.06.007
1359-6462/

that the vast majority of particles exhibit an elongated, non-equilibrium shape even after long anneals. This means that they did not reach the state of thermodynamic equilibrium, which is the main condition for applicability of the Kaischew–Wulff–Winterbottom analysis.

According to Nichols and Mullins, the equilibration time, τ, of a particle of radius r is [13]:

$$\tau = \frac{r^4 kT}{24\gamma D_s \nu \Omega^2} \quad (2)$$

where γ, D_s, ν and Ω are the surface energy, the surface self-diffusion coefficient, the number of mobile atoms per unit area of the surface, and the atomic volume, respectively. kT has it's usual thermodynamic meaning. However, the Eq. (2) describes the equilibration of the particle with a rough surface and is not applicable to faceted particles. In the latter case, the normal motion of the facet requires the nucleation of the new atomic layer on the facet. For the crystals larger than several nanometers in diameter the energy barrier associated with this nucleation becomes prohibitively high, which significantly increases the time of equilibration [14]. This is why the particles of sub-micrometer size can retain their non-equilibrium shapes for very long times at the temperatures slightly below the melting point of the metal [15]. An extraordinary stability of the faceted single crystal Au particles of non-equilibrium shapes was demonstrated in Ref. [16]. In the same system, the particles containing a grain boundary have readily evolved toward an equilibrium shape even after the shortest annealing time [17]. The main conclusion which can be drawn from these works is that the presence of defects allows alternative routes for the atomic transport and accelerates particles equilibration.

In this letter we experimentally demonstrate that mechanically-induced damage to the faceted particles produced by solid state dewetting significantly accelerates their equilibration, and provides a more efficient route to equilibrium as compared to long high temperature annealings.

Thin Au film was deposited on *c*-plane oriented polished sapphire substrate employing the e-beam deposition technique. The film was patterned employing the photolithography method and lift off procedure. Prior to the photo resist coating, a Au layer of 2 nm in thickness was deposited on the substrate as a reflective coating to improve the resolution of the exposed pattern. The second deposition of additional 28 nm of Au was performed after development of the pattern, so that the total thickness of the Au film was 30 nm. The sample was annealed in tube resistance furnace for 24 h at 900 °C in ambient air to cause the film dewetting and to form faceted gold particles (Fig. 1a). The morphology of the particles was similar to that observed in Refs. [8,10,16–17]. A number of selected particles was imaged with the aid of AFM (Park Systems XE-70) and high resolution scanning electron microscope (HR-SEM, Zeiss Ultra plus), and deformed with the aid of AFM-based indentation. The height of the particles, h, was measured by AFM in the intermittent-contact mode employing Si tips, and the projected area of the particles, A, was determined from the HR-SEM micrographs employing ImageJ software. The SEM imaging was performed without the use of conducting layers or tapes, in order to avoid contaminations and allow additional heat treatments after characterization. After the initial geometrical characterization, the AFM-based indentation of the selected particles was performed using the sharp diamond pyramidal probe attached to sapphire cantilever (Micro Star Technologies). Prior to indentation, the imaging with diamond tip was carried out in intermittent-contact mode. The scanning itself can produce significant damage to the particles (see Fig. 1s in the Supplementary Material) when the set point distance is much shorter than the value typical for the non-contact AFM mode. We used that

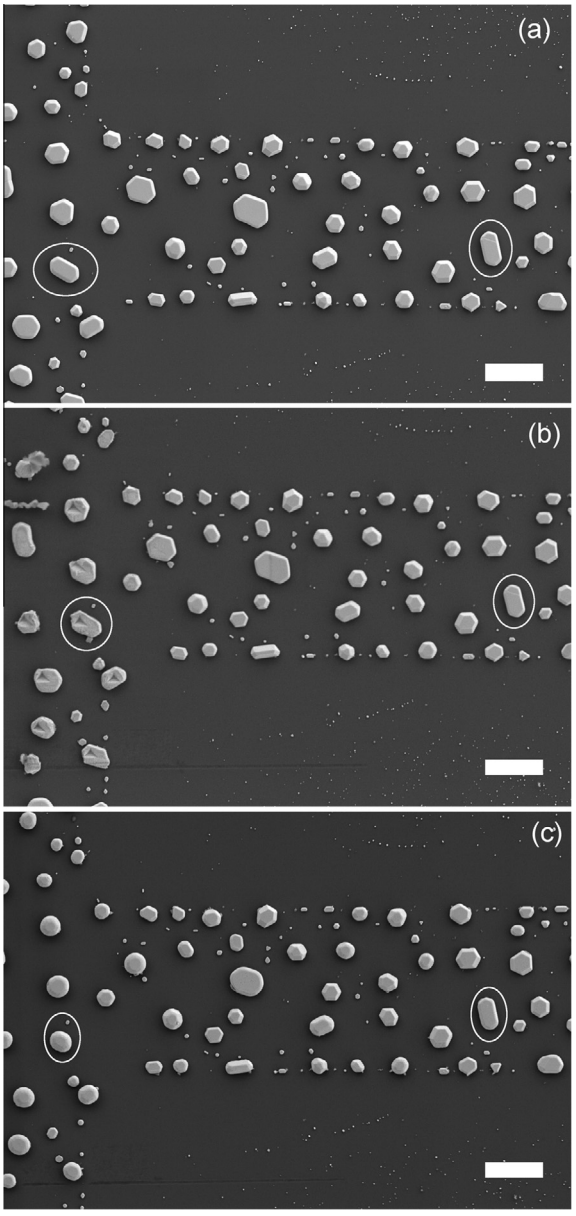

Fig. 1. SEM micrographs of one and the same region of Au thin film (a) after agglomeration of the film (b) after indentation (c) after additional heat treatment at 900 °C for 1 h in ambient air. Note the changing shapes of deformed particles on the left hand side, in comparison to the constant shape of pristine particles on the right hand side. Two representative particles which equilibrated after indentation, and which kept its initial non-equilibrium shape are marked on the left- and right-hand sides of the figure, respectively. The scale bars are 2 μm.

condition to increase the population of mechanically damaged particles. These "tapped" particles are considered separately in further analysis. The indentation was performed in load-control mode with maximum load up to 60 μN and the penetration depth up to ~100 nm, but never deeper than half of the particles height (see Supplementary Material). The particles were characterized after the indentation by AFM and HR-SEM, annealed in ambient air at 900 °C for 1 h, followed by additional characterization with the aid of AFM and HR-SEM (see Fig. 1b, c and Fig. 2s in the Supplementary Material).

The complete geometrical analysis before and after manipulations described above was carried out for 179 particles, of which 27 particles were subjected to indentation in AFM, 77 particles were damaged by scanning with diamond tip (tapped particles),