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Dynamics of gold clusters on amorphous carbon films induced by annealing in a transmission electron microscope

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Abstract

The change of the size distribution of Au clusters induced by annealing was studied in situ by transmission electron microscopy. Starting from statistically distributed Au clusters on a thin amorphous carbon film, "islands" are formed within a few months storage at room temperature, which consist of Au clusters with sizes <4 nm embedded in a thin Au film. These islands cover originally areas with sizes around $25 \times 70\ \text{nm}^2$. If the temperature is increased in the transmission electron microscope two different processes can be clearly distinguished that lead to the coarsening of the cluster size distribution: cluster coalescence and (contactless) Ostwald ripening. The degree and rate of the coarsening are found to depend on the underlying surface (Au film or amorphous carbon) and the exposure to the high-flux high-energy electron beam, which can be estimated to lead to high-temperature excursions in a cluster on a 10^{-12} s time scale. The experimental findings are confirmed by Monte-Carlo simulations using the many-body Gupta potentials in order to calculate the Au/Au interaction. Moreover, the results of MC simulations suggest an electron-beam induced formation of a "quasi-two-dimensional gas" of small highly mobile Au species on the Au film, which promotes Ostwald ripening.

Keywords: Au clusters; Au film; Ostwald ripening; Transmission electron microscopy; Monte-Carlo simulations

1. Introduction

Investigations concerning the stability of arrays of nanoparticles deposited on a substrate are of considerable interest with regard to potential applications in catalysis, nanoelectronics or nanooptics [1]. In technical applications the temporal behaviour of the particle size distribution and the interaction of particles with a substrate needs to be well understood because it strongly affects the functional properties of the particles, in some cases irreversibly [2–4]. In particular at elevated temperatures, a strong effect on the particle sizes must be expected. It is therefore highly relevant to study the effects of heating on nanoparticle arrays.

Ostwald ripening is a well-known phenomenon, which has been studied thoroughly in bulk alloy systems as one decisive process during the precipitation of a new phase [5]. The phenomenon is based on the Gibbs–Thomson effect according to which small precipitates have a higher "vapour pressure" than larger precipitates [6]. This causes a net flow of material from small to larger precipitates leading to the coarsening of the particle size distribution. Ostwald ripening has been also shown to occur for ensembles of nanoparticles focusing particularly on model systems like two-dimensional Ag islands on Ag(111) substrates [7].

Applying transmission electron microscopy (TEM) the dynamic behaviour of nanoparticles can be imaged conveniently with high spatial resolution. Clearly, the influence of the high-flux high-energy electron beam has to be considered if TEM experiments are performed [8,9]. TEM studies have revealed the existence of a quasimolten [10]

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state in which small Au particles change the shape and structure on a time scale of minutes or a few hours. The energy to initiate this unstable state is provided by the high-flux electron beam, by which the interaction of the particle with the substrate is reduced [11].

Recently, we have carried out transmission electron microscopy (TEM) experiments regarding the temporal behaviour of statistically distributed Au clusters with a diameter $d < 4$ nm deposited on amorphous carbon (a-C) films by laser ablation [12]. Experimentally, after a four months storage at room temperature it was observed that Au clusters embedded in a thin Au film with a typical area of 25×70 nm^2 are formed, which modify significantly the initial statistical particle distribution found immediately after the deposition. We will further denote the film with the embedded clusters as "islands". In Fig. 1a, a TEM image of Au clusters supported on an a-C film one day after the deposition is shown. Fig. 1b displays an island consisting of a continuous Au film (region with darker contrast compared to a-C film) with embedded Au clusters, which is formed after the sample was stored about four months at room temperature in a sealed container in air. A detailed analysis in combination with Monte-Carlo (MC) simulations revealed that the embedding Au film results most likely from diffusion and agglomeration processes of very small Au species, which stem from the cluster source operating without mass selection [12].

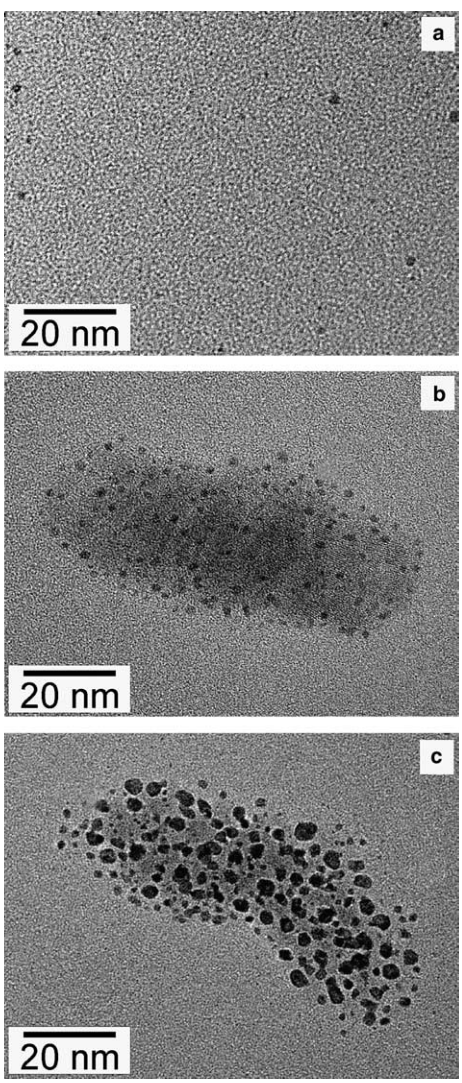

Fig. 1. TEM images of Au clusters deposited on an amorphous carbon substrate by laser ablation (3000 shots): (a) sample one day after its preparation, (b) sample about 100 d after its preparation and (c) sample about 100 d after its preparation and additional in situ annealing at 373 K for 2 h under exclusion of electron beam exposure.

In a first annealing experiment we observed coarsening phenomena when annealing the aforementioned Au films [12]. Fig. 1c illustrates how after 2 h of annealing at 373 K (i) the amount of Au forming the film is diminished (ii) the mean size of the particles is increased and (iii) the shape of the particles has become irregular.

In this study, we report detailed annealing experiments of the given Au island system investigated by TEM. The influence of the electron beam on the dynamics of the Au adsorbate system is shown and contrasted to the temperature effects. MC simulations are performed to obtain a microscopic understanding of the observed phenomena.

2. Experimental techniques and theory

2.1. Experimental techniques

The primary samples were prepared depositing Au clusters on commercial a-C films, which were produced by evaporation in a carbon arc by Arizona Carbon Foil Co., Inc. and distributed by Plano GmbH as type S160. These films are mounted on 200 mesh Cu grids. The thickness of the films is given by the manufacturer as 10–12.5 nm, its density is about 2.0 g/cm^3.

The Au clusters were collected from the primary beam of a laser vaporization cluster source, which has been described elsewhere [13]. In brief, the laser vaporization cluster source is a variant of the Smalley–deHeer-type [14] setup optimized by Heiz [15] for high yield. The source is equipped with a rotating Au disc target with a diameter of 50 mm, which is sealed with a teflon gasket against the source block. A pulsed laser (Neodym-YAG, Continuum, 532 nm, 30 Hz repetition rate) is focused through a nozzle onto the target. A pulsed valve (General Valve, 5 bar backing pressure of He), which is synchronized with the laser, quenches the vaporized atoms into clusters, which expand through the nozzle and a skimmer into an oil diffusion pumped vacuum chamber. Au clusters (and atoms) are deposited—however, without further mass selection—onto a TEM grid placed in the primary beam in a distance of about 40 cm from the nozzle.

TEM was carried out with a Philips CM200 FEG/ST electron microscope operated at an energy of 200 keV. Typical current densities are in the order of 100 A/cm^2. A Gatan 652 Double Tilt Heating Holder operated by a Gatan 901 SmartSet Hot Stage Controller was used to perform the in situ annealing experiments.