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The effect of heat-treatment on morphology and mobility of Au nanoparticles

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Abstract

In the present paper we investigate the effect of heat-treatment on geometry and mobility of Au nanoparticles (NPs) on Si substrate. Chemically synthesized Au nanoparticles with median diameter of 14 nm were annealed at 200°C, 400°C, 600°C and 800°C for 1 hour. Geometry changes from faceted towards more rounded shapes were observed already for 200°C and increased further for higher temperatures. According to Kinetic Monte Carlo simulations NPs become rounded through the minimization of the surface area and transitioning to lower energy surface types {111} and {100}. Next, NPs were manipulated with atomic force microscope and it was found that the higher is annealing temperature, the less energy was required to displace the particle. However, after treatment at 800°C particles became immovable. We attributed this surprising effect to diffusion of gold into Si and to the growth of SiO_2.

Keywords: Gold, nanoparticles, melting, AFM, manipulation

Introduction

Gold is one of the most prominent materials used for studies related to nanostructures. The small size and the enhanced properties of Au nanoparticles (NPs) compared to bulk gold makes them important for the development of novel applications including drug delivery [1], sensors [2], printing [3] and catalysts [4]. Due to relative inertness, geometrical diversity and ease of synthesis Au NPs are attractive model material for nanotribological manipulation experiments [5]–[12], and simulations [13]. Additional flexibility is provided by the ability to tune the properties of the NPs by varying the size [14], shape [14] and chemical composition of the outer layer covering the NP [5]. These modifications become especially important for tribological applications since they can affect the interfacial behavior during contact.

Nanoparticle shape is known to have a huge impact on the real contact area between NP and substrate [14]. The morphology and thus the contact areas of the NP can be tuned by changing the synthesis parameters [15]. For already synthesized NPs morphology can be changed by giving additional energy to the NPs by laser treatment [16] or by heating the NPs in an oven. Partial melting can be achieved at significantly lower temperature than the melting temperature of bulk Au [17].

In scope of this study chemically synthesized faceted Au NPs were annealed at different temperatures ranging between 200-800°C, resulting in rounding of the NPs. The particles were then displaced with an atomic force microscope (AFM) in order to study the effect of annealing on their tribological behavior.

Experimental setup

NP synthesis

The colloidal suspension of Au NPs was made by reduction of an aqueous solution of $HAuCl_4 \cdot H_2O$ (*Sigma Aldrich*). Procedure consisted in adding 3 mL of 1% aqueous $HAuCl_4$ (*Sigma Aldrich*) to 150 mL of pure H_2O at 90°C with vigorous stirring, followed by addition of 2 ml of 1% aqueous solution of sodium citrate (Sigma Aldrich) one min later to stabilize the suspension. By reducing $HAuCl_4$, sodium citrate imparts the negative charge of the citrate ions to the Au NP surface [18],[19]. The solution was stirred for 5 min and then stored at 4 °C until needed [10].

Annealing

The silicon wafers (100, n/phosphorus doped, 3-6 ohm·cm, *Mat-Technology*) were cleaned with ethanol and the NPs were deposited by drop-casting. The drop dried in ambient conditions. Five samples with Au NP on Si wafer were prepared and four of them were then separately annealed in an oven for one hour at 200°C, 400°C, 600°C and 800°C, and one left untreated. Separate samples were prepared on heat resistant 50 nm silicon nitride support films (Pelco, Ted Pella) for transmission electron microscope (TEM) for acquisition of TEM images after heating to different temperatures.

Characterization

Morphology on NPs annealed at different temperatures was studied with TEM (ARM200, JEOL). A Null-Ellipsometer (Multiskop, Optrel, Germany), equipped with a 532 nm wavelength laser (Nd-YAG laser) was used for SiO_2 layer thickness measurements.

AFM setup

NP manipulations were performed with Bruker Multimode 8 AFM with the Peakforce Quantitative Nanomechanics (PeakForce QNM) mode using a rectangular AFM cantilever (Bruker, RTESPA-300, k=40 N/m) with resonance frequency around 300kHz.

Prior to each manipulation the samples were heated to 100°C to remove excess water. At first an image was taken with the high resolution QNM mode to find the Au particles. Then the operation mode was switched to the tapping mode. The oscillation amplitude was kept constant with feedback loop on and the power dissipated during tapping was calculated with the following formula [20]:

$$P = kf_0(A_{set}A_{piezo}\sin\theta - \frac{A_{set}^2}{Q}),$$

where k is cantilever spring constant, f_0 is the resonance frequency of the cantilever, A_{set} is the setpoint amplitude, A_{piezo} is the drive frequency, θ is the phase signal and Q is the quality factor of the AFM cantilever. Dissipated power was used as a measure of NPs mobility.

After each scan the force applied on the NPs was increased until all the particles in the area were displaced or the force was high enough to start severely damaging the tip. If the tip was too dull for performing manipulations the tip was replaced with a fresh and sharp AFM tip.

Simulation setup

Simulations of NP rounding were carried out using the Kinetic Monte Carlo (KMC) code Kimocs [21], which is specifically designed for metal surfaces. The parameters for Au, developed in [17], used the tethering method for stabilization [22].

Two sizes of initially cubic nanoparticle were used: 2 nm and 5 nm in diameter. Both types of particles were simulated at 726.85 °C (1000 K) in order to reduce the computational time. In the diffusion model used in Kimocs, computational time increases exponentially with decreasing temperature, making experimental temperatures unfeasible. Nevertheless, the temperature used in the simulations is significantly below the melting temperature of Au. Furthermore, in the computational model, the dynamics of the diffusion are unaffected by temperature, making comparisons to experimental results possible [21].

Visualizations of simulation results were generated with Ovito [23].

Results and discussion

According to TEM observations untreated Au NPs had irregular faceted shapes with diameters ranging from approximately 10 to 20 nm for most of the particles with median diameter of 14±2.3nm (measured on 40 particles). Typical TEM image of as-synthesised Au NPs is presented in Figure 1.

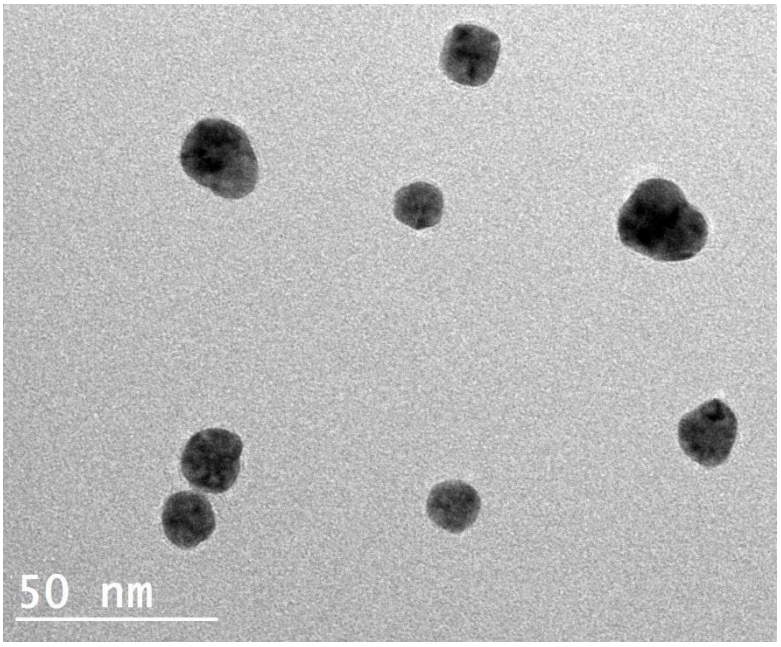

Figure 1. Typical TEM image of Au NPs before thermal treatment.

Influence of temperature – change in morphology

TEM observation revealed considerable changes in geometry of NPs towards more rounded shapes as a result of annealing although temperatures were far below melting point of bulk Au (1064 °C). Figure 2 presents typical TEM images taken from NPs annealed at different temperatures. Some tendency to rounding can be noticed already for sample annealed at 200ºC. Effect becomes clearly prominent for 400ºC and increases further for higher temperatures.

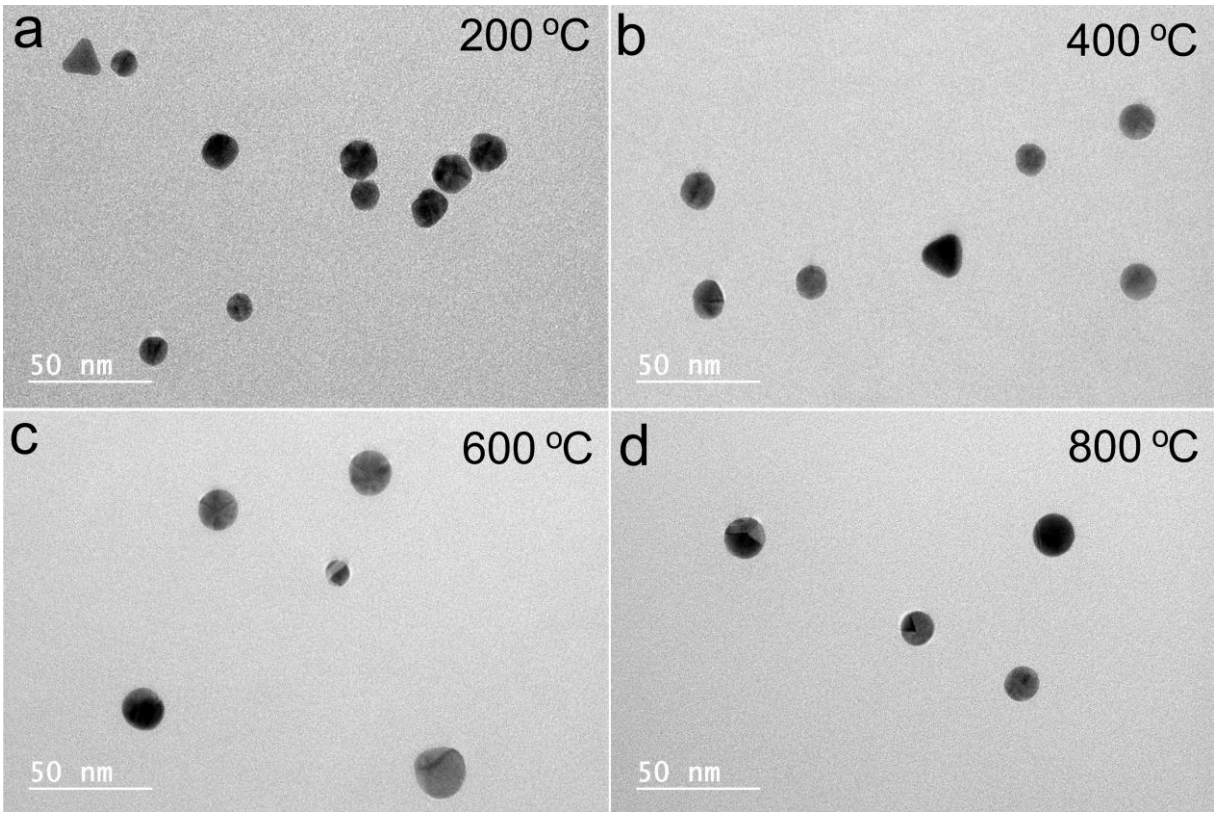

Figure 2. Morphology of Au NPs without annealing (a) and after annealing at 200°C (b), 400°C (c), and 800°C (d). A slight rounding of NPs can be seen at higher temperatures.

Reduced melting temperature for nanoparticles is not a new phenomenon. Already in 1976 Buffat and Borel demonstrated that the melting temperature of Au NPs is size dependent [24]. However, the decrease in melting temperature presented in their work was only up to few hundred degrees for particle diameters around 5 nm and was even less pronounced for larger particles approaching bulk values above 20 nm. In contrast, we observed rounding at much lower temperatures and even for particles exceeding 20 nm in diameter. Moreover, rounding of Au NPs at just 500ºC was reported even for particles exceeding 100 nm in diameters [6]. In case of rounding, it is probably more appropriate to speak about surface atoms diffusion instead of complete melting. Another important factor for heat-induced morphological changes overlooked by many other studies is annealing time. We believe it is rather surface effect resulting in rounding of NPs as an energy minimization via rearrangement of surface

atoms similar to effect demonstrated recently by Vigonski et al [17] for heat-induced segmentation of Au nanowires at temperatures much below Au melting point. It was noticed that effect of rounding was more pronounced for NPs with five-fold twinned inner structure in comparison to single crystalline particles in the form of truncated triangles. This can be explained by the presence of inner stresses stored inside five-fold twinned NPs and tendency of such particles to look for mechanism of stress relaxation [25]. Rearrangement of surface atoms into more rounded outer geometry can be a way for energy minimization of NPs while preserving five-fold twinned inner structure as shown for Au NPs heated to 800^{o}C in Figure 3.

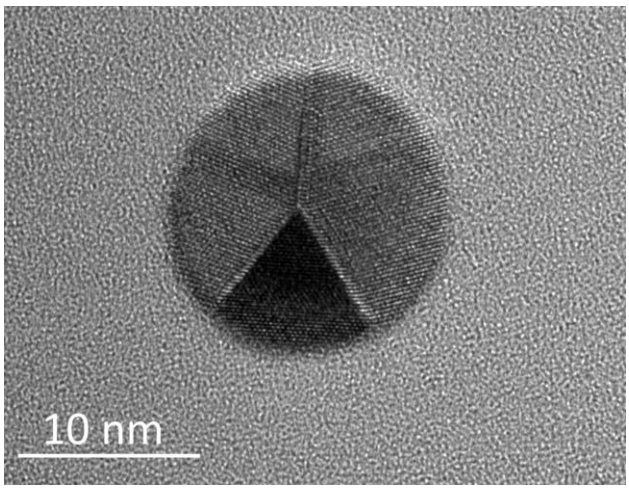

Figure 3. Au NP annealed at 800°C with well-pronounced five-fold twinned inner structure.

KMC simulations of diffusion at 726.85 °C (1000 K) show that NPs become rounded through the process of surface energy minimization that is realized through a combination of minimizing the surface area and transitioning to lower energy surface types (see Figure 4 and corresponding video in supporting data). The preferred surface for FCC materials such as Au is {111}, and simulations clearly show that the surfaces of this type grow as the nanoparticle relaxes. The KMC model used here describes perfect crystals, therefore the resulting shape resembles a dodecahedron bounded by the energetically favorable surfaces {111} and {100}. Our simulations do not include five-fold twinned particles and lower temperatures in favor of saving computational power and time. Advanced modelling and in-depth theoretical analysis of the rounding process lie outside the resent study and should be a basis of separate research. Nevertheless, this relatively simple model agrees well with results of our experiments and sheds light on processes that take place in small metal particles at elevated temperatures.

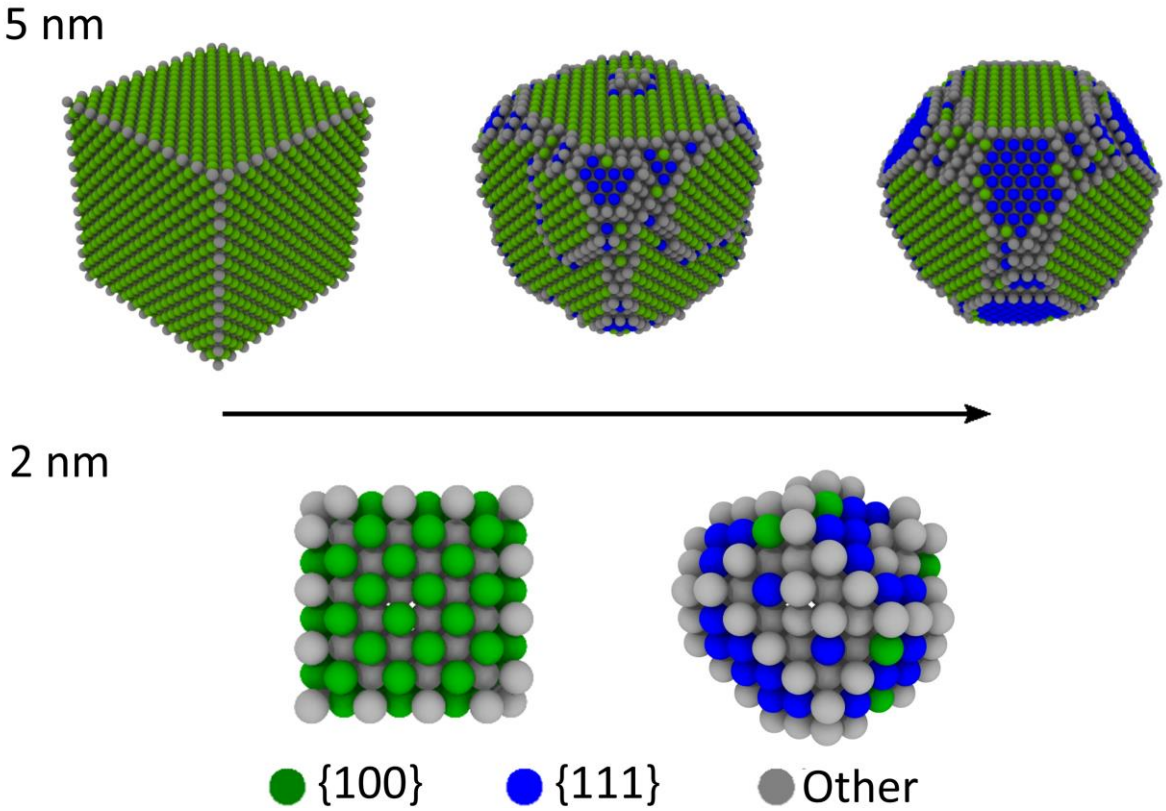

Figure 4. Transition of 5 nm (a) and 2 nm (b) nanoparticles into rounded shapes bounded by energetically favorable surfaces. Atoms are colored according to their crystallographic surface type.

Manipulation of Au NPs

The main goal of this paper was to investigate the effect of heat-induced rounding of Au NPs to their mobility. Rounding of NPs should result in decreased contact area in comparison to faceted particles and hence reduction of friction forces in accordance to know relation $\tau=F/A$ [6], where τ is a contact strength, F is friction force and A is contact area. For a round particle contact area is determined by contact mechanics methods [14], [26] and for perfect sphere it can be two orders of magnitude smaller than for a polyhedron-like NP as was shown in Vlassov et al [6].

Mobility of Au NPs was calculated with the dissipated power method that was previously shown to be effective technique for evaluation of NPs mobility in tapping mode AFM [10]. Example of manipulation sequences for the sample annealed at 400^{o}C is given in Figure 5. Selected area is scanned in tapping mode and the driving amplitude is increased until displacement of NPs is observed. Dissipated power is then calculated.

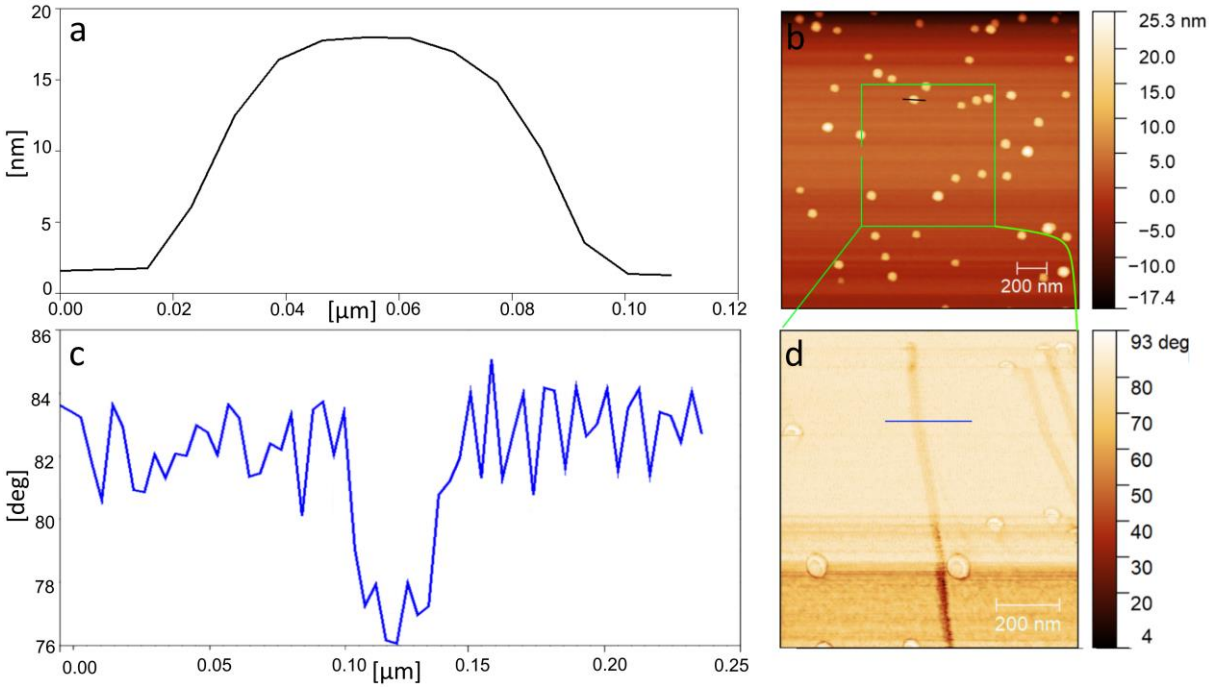

Figure 5.Topography image (B) and profile of Au NP (A) prior to manipulation. During the manipulation phase image (D) was recorded. D is profile of phase image.

In total 34 data points were collected - 12 measurements for NPs annealed at 600°C, 16 for NPs annealed at 400°C and 4 for NPs annealed at 200°C (Figure 6). The low amount of data points for 200°C is due to the fact that most of the NPs required more power for displacement than the experimental setup could provide. Therefore, actual average friction for 200°C is even higher. The energy required to displace NPs is the highest for particles annealed at 200°C and lowest for NPs heated at 600°C. This finding agrees well with rounding observed on TEM images.

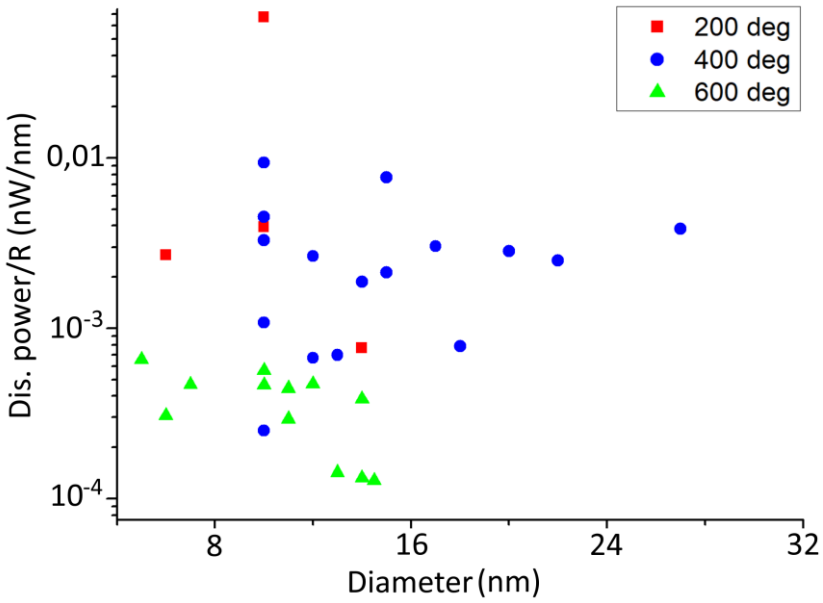

Figure 6. Dissipated power per NP radius vs NP radius.

Displacement of unannealed, as well as NPs annealed at 800°C was not possible. Immobility of unannealed NPs can be linked to more pronounced facets (and hence higher surface area), as well as the presence of surfactant that can act as a glue. Immobility of NPs heated to 800°C was surprising, especially considering the fact that they look the most round on TEM images. Possible explanation can be related to partial diffusion of Au into Si substrate. It is known, that gold diffuses into silicon at higher temperatures by the so-called kick-out mechanism, in which self-interstitials present in thermal equilibrium displace substitutionally dissolved Au atoms into interstices, so that these may undergo rapid interstitial diffusion [27]. The process is highly temperature dependent and diffusion at 800^{o}C is four order of magnitude higher than at 400^{o}C (See Table 7 in [28]). Another reason may be related to the temperature-sensitive growth of SiO_2 layer [29] that escalates rapidly above 600^{o}C as can be seen from ellipsometry measurements presented in Figure 7. How exactly the rapid growth of SiO_2 layer may be related to drastic increase in friction remains unclear and can be the subject for future studies. Overall, we demonstrated that heat treatment, which is widely used as a surfactant removal step prior to nanomanipulation experiments, can have extensive effect on mobility of Au NPs.

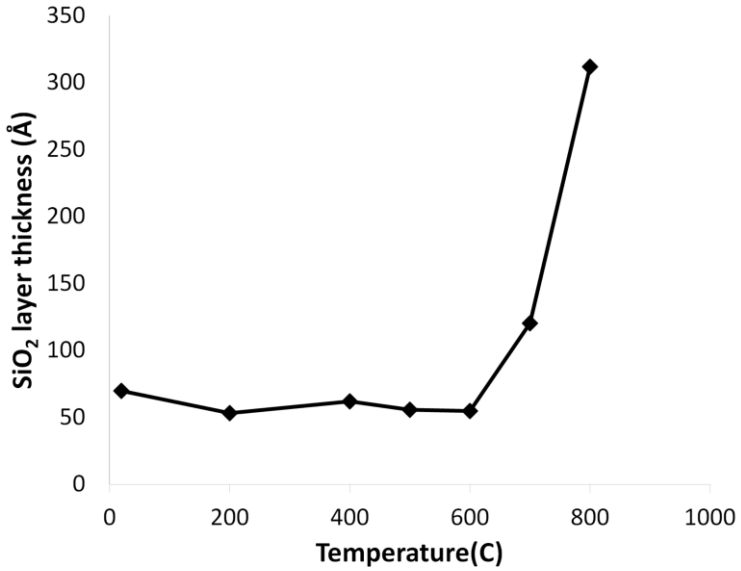

Figure 7. Evolution of the SiO_2 thickness as a function of temperature.

Conclusions

Chemically synthesized Au nanoparticles with median diameter of 14 nm were annealed at 200°C, 400°C, 600°C and 800°C for 1 hour. Untreated particles had irregular faceted shapes. Annealing resulted in geometry changes towards more rounded shapes. Slight tendency to rounding was noticed already for 200^{o}C. Effect became clearly prominent for 400^{o}C and increased further for higher temperatures. After 800^{o}C most of the particles had sphere-like shape. KCM simulations of diffusion at 726.85 °C (1000 K) show that NPs become rounded through the process of surface energy minimization that is realized through a combination of minimizing the surface area and transitioning to lower energy surface types {111} and {100}. Next, nanoparticles were manipulated with AFM. It was found that the higher is annealing temperature, the less energy was required to displace the particle. However, after treatment at 800°C particles became immovable. We attributed this surprising effect to diffusion of gold into Si and to the growth of SiO2. Both processes are highly temperature dependent exhibiting

drastic increase of intensity above 700°C. Overall, we demonstrated that heat treatment, which is widely used as a surfactant removal step prior to nanomanipulation experiments, can have extensive effect on mobility of Au nanoparticles.

Acknowledgements

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