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Temperature-induced processes for size-selected metallic nanoparticles on surfaces

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ABSTRACT

The melting behavior of Iron-Nickel alloy nanoparticles on W(110) was studied under UHV conditions as a function of heating temperature and heating duration. These particles were found to be stable at 423 K without evaporation or diffusion taking place. Unrolling carpet behavior occurs at higher temperatures. This creates ramified islands around the nanoparticles. Ostwald ripening at higher temperatures or longer heating times is creating compact islands. The melting of these nanoparticles opens the possibility for thin film growth of FeNi alloys. The formation of monolayer high islands is a strong contrast to Fe, Co, and FeCo alloy nanoparticles which are dominated by direct evaporation, single atom surface diffusion and anisotropic spreading.

1. Introduction

The size range between bulk material on the one hand and single atoms on the other hand is giving nanoparticles a unique set of properties and fascinating behavior. Having been under investigation for a long time, the materials and size are obviously important contributors to these properties. These also include the melting point and other thermodynamic characteristics. The stoichiometry is another important factor when dealing with alloy systems.

While it is possible to grow nanoparticles directly on a substrate, our work is based on the creation of nanoparticles from the gas phase and their subsequent deposition.

Previous research includes the crystallization and alignment of iron particles during deposition [1] and their thermal treatment [2,3]. While thermal treatment typically takes place on a scale of minutes and longer, the deposition and subsequent relaxation lasts only pico- to nanoseconds. Therefore the fine tuning of the kinetic energy is offering a different approach to the treatment of nanoparticles. The additional energy can lead to a complete recrystallization on impact within picoseconds [4].

In this contribution size selected supported nanoparticles made of iron-nickel alloy being prepared under UHV conditions and investigated in-situ by scanning tunneling microscopy will be discussed. This extends our previous work concerning temperature induced effects of transition metal nanoparticles on W(110).

2. Materials and methods

2.1. Nanoparticles

Nanoparticles are generated in an Arc Cluster Ion Source (ACIS) [5] with a typical size between 5 and 15 nm. It consists of a hollow cathode which is made from $Iron_{0.5}Nickel_{0.5}$ alloy. Argon is injected in the back of the cathode. An arc discharge strikes the inner wall and removes metal. The Argon gas leaves the cathode through a small nozzle and is taking the metal vapor with it. The gas is cooled in a supersonic expansion. Two skimmer stages with a roots and turbomolecular pump respectively remove argon gas and shape a narrow beam of nanoparticles. The additional injection of Helium can improve the cooling process.

A high amount of singly charged particles in the beam and the narrow velocity distribution of the super-sonic expansion facilitate mass selection by a static electric field. This field is created in a quadrupole deflector with a maximum voltage of ±2 kV. The best possible mass resolution is $\Delta M/M = 10\%$. The first pumping stage can be throttled to widen the velocity distribution. This allows for a wider mass distribution. Particle flux can be monitored at a grid after deflection. The subsequent deposition fulfills soft-landing condition at a kinetic energy below 0.1 eV per atom. The pressure

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in the deposition chamber is in the 10^{-7} mbar regime during ACIS operation.

2.2. Substrate preparation

The substrate for nanoparticle deposition is a tungsten single crystal with a (110) surface. Well known cleaning procedures are outlined by e.g. Bode et al. [6]. The W(110) crystal is cleaned before deposition in a separate chamber by electron bombardment heating (flashing) at $T > 2000$ K and $p_0 < 5 \times 10^{-10}$ mbar. Carbon impurities are removed by oxygen annealing at $T = 1500$ K and $p_{oxygen} = 10^{-7}$ mbar. Temperature is determined by narrow band pyrometric measurement at wavelength of 960 nm and emissivity of $\epsilon = 0.3$.

A resistive heater is integrated into the manipulator of the STM chamber. This allows tempering of samples between 350 K and 1100 K.

2.3. Scanning tunneling microscopy

The nanoparticles are investigated in situ by means of scanning tunneling microscopy (STM). The microscope is a MicroSPM by Omicron. Base pressure is below 3×10^{-10} mbar. All measurements are done at room temperature.

STM gives easy access to the height of nanoparticles in the size regime of ACIS. Additional information can be obtained about the structure of the top-facets. Determination of lateral size is limited due to tip-surface convolution. XY-calibration and image-distortion were checked on carburized W(110). The R(15 × 3) reconstruction exhibits thin lines with a separation of 1.37 nm that are aligned at ±35° with respect to the W[001] axis [7]. Axis orientation was cross-checked by LEED while x-calibration is in perfect agreement with measurements of HOPG. Slow scanning speeds (typically 1000 nm/s at 1000 nm image size) were employed to keep the tip from crashing into nanoparticles and for providing low-drift conditions. Z-calibration is based on the well-known step height of W(110).

3. Theory

The melting properties of nano-scaled systems were previously investigated. A behavior that is often observed is known as unrolling carpet. I.e. a layer of atoms forms around the nanoparticle or dot during melting. Reuter et al. [8] have shown this behavior for tempering of iron, nickel and cobalt dots that were grown on W(110). Similar behavior has been found for deposited iron nanoparticles. Other systems, like Pd [9] exhibit similar properties.

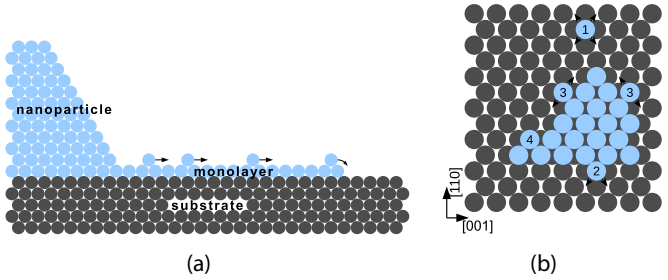

Fig. 1. Hard ball model for surface diffusion of islands. Unrolling carpet mechanism: (a) Atoms from the nanoparticle are moving on top of the monolayer until the reach it's edge. Adapted from [8]. Anisotropic diffusion on bcc(110): (b) The free atom (1) can move along the ⟨111⟩ axes. Atom (2) may detach from the island. Atom (3) may move along the island until it reaches position (4). Adapted from [10].

The effect is driven by a strong interaction between substrate and the first monolayer whereas the interaction between first and second monolayer is comparably weak. The first monolayer is therefore stable. Single atoms from the central nanoparticle are transported by diffusion until they reach the edge of the first monolayer (see Fig. 1(a)). The monolayer is spreading because these atoms are subsequently trapped at the step edges.

One factor that contributes to the shape of islands is the crystallographic structure of the substrate. Köhler et al. [10] describe a model for an anisotropic spreading of islands on a bcc(110) surface. The ⟨111⟩ axes are the easiest directions for hopping between adsorption sites (see Fig. 1(b), atom (1)). Hopping along the ⟨001⟩ direction is rather unlikely because it leads over an on-top position. I.e. an atom (2) that is attached at a ⟨110⟩ edge of an island will probably detach from the island while atoms (3) at ⟨111⟩ edges can move easily along the edge until they reach a relatively stable site with multiple nearest neighbors (4). Therefore islands are elongated along the [001] axis.

4. Results

$Fe_{0.5}Ni_{0.5}$ nanoparticles were deposited on W(110) and subsequently heated. This section will discuss the properties of these nanoparticles after deposition and their response to elevated temperatures.

4.1. Softlanding

Fig. 2(a) shows the size distribution for different source parameters. Both the first stage pumping speed and the deflection voltage were varied. The nanoparticles considered for further treatment

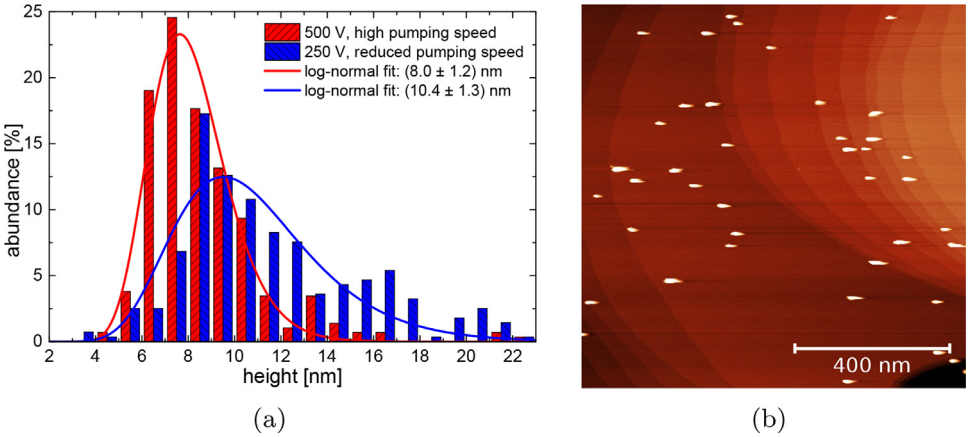

Fig. 2. FeNi nanoparticles after deposition on W(110). (a) Height distribution for different source parameters. (b) STM image after deposition at reduced pumping speed. No preferred landing sites (+1.0 V, 0.8 nA).

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