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Evaporation of silicon nanoparticles under scanning tunneling microscope control

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ABSTRACT

A kinetic model is developed to describe the heating and evaporation of a spherical nanoparticle under the influence of a scanning tunneling microscope (STM). Simulations were performed for silicon nanoparticles of different sizes and for different STM parameters. Different kinetic features of evaporation are predicted and discussed. The lifetime of the nanoparticles is estimated and compared with original experimental data obtained for layers of silicon nanoparticles formed upon magnetron sputtering and deposited on a highly oriented pyrolytic graphite surface (HOPG).

1. Introduction

Silicon nanoparticles have a broad field of interest. Recent work describes their use in photonic and photovoltaic applications [1–3] also referring to quantum dots or silicon nanocrystals. Silicon nanocrystals have also been applied as fluorescent biological labels where their benefit compared to other fluorescent probes lies in the narrow and tunable emission spectrum as well as in the photochemical stability [4–6]. Silicon nanoparticles are also used in smart textiles, for example to create superhydrophilic wool by coating [7]. Silicon is also the raw material of information technology [8–10]. A main goal of this field is to store information in the smallest possible regimes. Nanolithography is a major technology for the manipulation of surfaces at the nanometer scale. Scanning probe lithography by means of an Atomic Force Microscope is already well-established. Dip-pen lithography [11,12], and local oxidation nanolithography also often work on silicon [13] and are the two most common techniques in this area. With such techniques, single atoms can be pulled or pushed over a surface [14] and aligned in certain ways. For example, Cu(1 1 1) surface state electrons could be confined by positioning 48 iron atoms in a circular coral [15]. Feedback-controlled lithography is a well-known technique often used in combination with atomic manipulation. In it, the field emission current from the tip is used as the feedback signal to control the spacing to the sample. It has been used to induce chemical reactions [16–18], create molecular switches [19,20] and induce single-bond breakage [21] and formation [22]. Scanning tunneling lithography may also be realized by local heating induced by tunneling electrons. Recently, thermal decomposition of C_{60} [23] by resonant electron heating of C_{60} in the junction of a STM has been reported, also discussing the effect of inelastic electron scattering [24]. STM manipulation of layers formed by silicon or titanium nanoparticles deposited on HOPG with the help of magnetron or hollow cathode sputtering has been reported in the literature [25–28]. The nanoparticles form homogeneous films, possibly consisting of several layers, with radii from 2.5 to 5.5 nm. Both an increase in the bias voltage and in the tunneling current trigger a manipulation of the nanoparticles below the STM tip. The manipulation at an increased tunneling current [25,26] was found to be most promising operational mode. It results in sharp structures of reduced brightness and lower corrugation. Controlled evaporation of the nanoparticles is a possible explanation for this process which offers good prospects for scanning tunneling lithography. Such experimental findings call for detailed theoretical explanations in order to gain more insight into the underlying processes and to explore and develop future applications. In the present work we develop a robust model that describes the evaporation of nanoparticles under STM control.

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The paper is organized as follows. The model and some computational details are described in Section 2. The results of simulations and experiment are reported in Sections 3 and 4. Some concluding remarks can be found in Section 5.

2. Model and computational details

Further we assume the coexistence of two phases: in the first phase temperature increases due to inelastic excitation (without vaporization taking place) and is primarily given by the heating power divided by the heat capacitance. In the second phase the material evaporates with almost constant flux. It should be stressed from the very beginning that the material which is vaporized in experiment from the film is atomic silicon which covers the existing structures with a thin layer and does not look as big particles of lumps. Part of the material sticks to the STM tip (further back, as it does not reduce the resolution) or may be even pumped away. Only in very rare cases where we operated with very high current during the writing process, we find some high lumps of debris up to a few 100 nm away from the pit we just formed. This indicates indeed that material is adsorbed on the tip.

To model the time-dependent mass and heat balance, it is convenient to introduce a system of two differential equations describing the dynamics of two key parameters: the number of evaporated atoms (N) and the local temperature of the particle (T):

$$\begin{cases} \frac{dN}{d\tau} = S\upsilon \\ \frac{dT}{d\tau} = \frac{I\phi_{bias} - \upsilon S\, dH_a - S\varepsilon\bar{\sigma}T^4 - \Delta Q_{exch}}{c_p(N_0 - N)} \end{cases}, \tag{1}$$

where N_0 is the initial number of atoms in a nanoparticle, τ is time, υ is the evaporation flux. I is the tunneling current, ϕ_{bias} is the bias potential, $S = 2\pi r^2$ is the surface area of a hemisphere of radius r modeling a particle, dH_a is the size-dependent atomization energy of the nanoparticle, ε is the emissivity coefficient (which was assumed to be 0.9), $\bar{\sigma}$ is the Stefan–Boltzmann constant (5.67×10^{-8} J s^{-1} m^{-2} K^{-4}) ΔQ_{exch} is the heat exchange term (see Eq. (11)).

For simplicity, in Eq. (1) a hemispherical geometry is used to describe the single nanoparticle from which atoms evaporate (see Fig. 1). Another choice would, however, not qualitatively affect the observed effects. A simple equation to calculate the evaporation flux υ takes the form [28,29]:

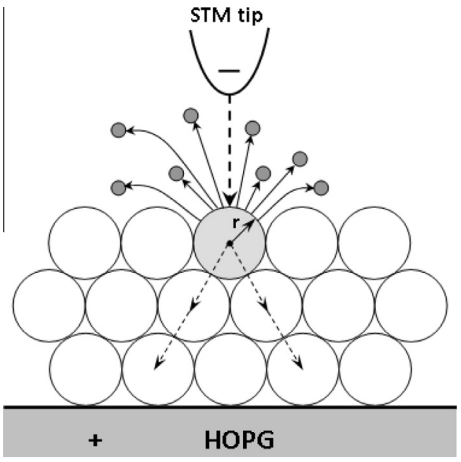

Fig. 1. Scheme illustrating the evaporation of a silicon nanoparticle induced by a tunneling current (dashed arrows show possible direction of current). The evaporating nanoparticle is represented by a sphere of radius r and resides among other neighbors forming layers at the HOPG surface.

$$\upsilon = \frac{p_s}{\sqrt{2\pi M k_B T}}, \tag{2}$$

where p_s is the vapor pressure on the surface of a particle, T is the local temperature of the particle and M is the atomic mass.

To address the change of pressure near a sphere of radius r due to the surface curvature, the following equation can be used (see its derivation if Ref. [30])[1]:

$$\ln\left(\frac{p_s}{p_s^0}\right) = \frac{2V_m\sigma}{rRT}, \tag{3}$$

where p_s^0 is the vapor pressure over the flat surface of solid, V_m is the molar volume of the substance (the nanoparticle material), σ is its surface tension factor (0.85 J m^{-2} for solid Si [31]) and R is the gas constant.

On the basis of the ideal gas equation we have,

$$p_s^0 = n^* k_B T, \tag{4}$$

where n^* is the concentration of atoms in the vapor.

We also assume that the evaporation of a nanoparticle (except at the very end of this process) occurs in a steady-state regime, i.e. a local thermodynamic equilibrium is achieved rapidly. Then the concentration n^* is calculated in the usual way:

$$n^* = n^0 \exp(-\Delta G_a / k_B T), \tag{5}$$

where n^0 is the concentration of atoms in perfect crystalline silicon (5.01×10^{28} m^{-3}) and ΔG_a is the Gibbs energy of evaporation (atomization).

In turn, we have

$$\Delta G_a = \Delta H_a - T\Delta S_a, \tag{6}$$

where ΔH_a and ΔS_a are the atomization enthalpy and entropy, respectively.

In further calculations we take into account the temperature dependency of both quantities:

$$\Delta H_a = \Delta H_a^0 + c_p(T - T_0), \tag{7}$$

and

$$\Delta S_a = \Delta S_a^0 + c_p \ln(T/T_0), \tag{8}$$

where T_0 is the ambient temperature (298 K), c_p is the heat capacity of particle, ΔH_a = 468.1 kJ mol^{-1} and ΔS_a^0 = 149.1 J K^{-1} mol^{-1} [31].

Considering the second equation of (1), the first term in the numerator ($I\phi_{bias}$) appears in accordance with the Joule–Lentz law; it describes the heat gain due to the tunneling current. The electro-conductivity of layers consisting of silicon nanoparticles was investigated in Ref. [32]; the author proposed a jump mechanism which can be described in terms of the Mott theory.

It was observed experimentally (see, for example, Refs. [33,34]) that contributions to current significantly depend on the size of a silicone tunneling junction. Total current (I) can be recast as a sum:

$$I = I_{el} + I_{in}, \tag{9}$$

where I_{el} and I_{in} are elastic and inelastic components.

The inelastic current strongly depends on electron–phonon interaction (see theory in Refs. [35,36]). The release of an energy excess in this case results in the heating of a tunneling junction (the Joule–Lentz law). On the contrary, the elastic current does not lead to any heating. Introducing a coefficient ξ ($0 < \xi < 1$) we can write:

$$I = \xi I + (1 - \xi)I. \tag{10}$$

[1] Although the surface tension of nanoparticles depends in general on their size, we did not address this effect for simplicity in further calculations.