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Metal nanostructure growth on molecular buffer layers of CO_2

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Abstract

Buffer-layer-assisted growth (BLAG) occurs when a multilayer of condensed gas acts as the surface on which impinging atoms form clusters that subsequently diffuse and coalesce during buffer desorption. We investigated Au, Cu, and Ni nanostructure formation using buffer layers of solid CO_2 and compared the results to what has been found for solid Xe buffers. The cluster densities could be controlled from $\sim 10^8$ to 10^{12} cm^{-2} by taking advantage of the power law dependence of density on the buffer layer thickness. For Au and Cu, the crossover from compact to ramified structures could be followed. For Ni, even small particles were ramified. The effective activation energies for diffusion of large ramified clusters on CO_2 were determined to be 0.91, 1.02, and 0.93 eV for Au, Cu, and Ni, respectively. These are significantly higher than those observed on Xe, and they reflect the higher polarizability of CO_2. The diffusion prefactors increased exponentially with the increase in diffusion barrier, demonstrating a Meyer–Neldel compensation effect. The characteristic energy of this process, 9 meV, was higher than for Xe due to the more energetic phonons of CO_2. It is comparable to the energies of buffer phonons active during buffer desorption, revealing that cluster motion on CO_2 is a many-body process fueled by coincidence of activated buffer phonons.

Keywords: Clusters; Growth; Surface diffusion; Carbon dioxide; Molecular solids

1. Introduction

There is much interest in the controlled synthesis of supported nanostructures of specific sizes and shapes, interest that is related to the novel

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and potentially important properties of such structures. Recently, Huang et al. [1] introduced a technique for synthesis, based upon earlier work by Waddill et al. [2,3], that used a solid rare gas buffer layer to isolate the substrate from adatoms delivered by physical vapor deposition to the surface of the buffer. The weak interaction between the deposited material and the buffer allowed cluster nucleation, and the desorption of the buffer activated cluster diffusion and aggregation. This technique, termed buffer-layer-assisted growth or BLAG, is unique in that it avoids adatom interaction with the substrate and allows for the delivery of a wide range of pristine clusters on any given substrate.

BLAG was originally used to grow defect-free, abrupt metal–semiconductor interfaces [2,4]. Later, Huang et al. [1] recognized that the density of Ag particles delivered to Si(1 1 1)-(7 × 7) depended sensitively on the thickness of the buffer layer. Haley and Weaver [5] quantified this dependence and showed a power law dependence that agreed well with simulations of diffusion-limited cluster–cluster aggregation [6]. The physics of cluster diffusion on an incommensurate rare gas buffer was investigated by Antonov et al. [7,8] through studies of the growth of metal particles on Xe, Kr, and Ar. They demonstrated that cluster diffusivities varied as $D(S,T) = D(S)D(T)$ where $D(S)$ describes the cluster size dependence and $D(T)$ reflects the temperature dependence. Significantly, $D(S)$ was inversely proportional to the particle–buffer contact area S. The effective activation energies and pre-exponential factors associated with $D(T)$ were determined for clusters of several different metals on Xe, and a compensation effect [9] was discovered that related the energies and the pre-factors. Particle diffusion was then ascribed to many-body processes with the phonons of the buffer providing the needed energy.

In this paper, we focus on BLAG where the buffer layer is solid carbon dioxide and the nanostructures of interest are Au, Cu, and Ni. This extends previous work to a molecular buffer to demonstrate a broader generality of the technique. It also determines similarities and differences associated with higher desorption temperatures, a more complex metal–buffer interface, and lower symmetry in the solid buffer. As discussed below, the observed dependence of cluster number density on buffer layer thickness was strikingly similar to those found for BLAG on rare gas buffers. Pre-exponential factors for diffusion were several orders of magnitude larger than those for Xe, while effective activation energies were also larger by about a factor of 2. As observed in metal cluster diffusion on Xe [8], we find an exponential dependence of these pre-factors on activation energy that reflects the phonon energies of solid CO_2 activated during buffer desorption at ~90 K. Our results suggest that buffer materials that desorb at even higher temperatures than CO_2 may also give rise to nanoparticle formation.[1]

2. Experiment

Sample growth was done in a chamber operating at base pressures of $<1 \times 10^{-10}$ Torr. The substrates were 20–30 nm films of amorphous carbon (a-C) supported by Cu grids. They were cooled to ~20 K using a closed-cycle He refrigerator. The temperature was measured with a AuFe–Chromel thermocouple attached to the cold head. The buffer growth rate was determined from $I = p/(2\pi mkT)^{1/2}$ where I is the flux of incident molecules per unit time per unit area, p is the CO_2 partial pressure of 1×10^{-6} Torr, m is the molecular mass, and T is ambient temperature. The sticking coefficient was assumed to be unity, and the thickness was controlled by the time of exposure. Once the buffer was formed, the metals were vapor deposited from resistively heated sources (W baskets for Au and Cu and alumina-coated W baskets for Ni) with typical deposition rates of 0.02–0.05 Å/s. The amount deposited was measured with a quartz microbalance. While the amount is given in Ångstroms, referenced to the bulk parameters of the metals, we emphasize that the deposited

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[1] Growth of a CO_2 buffer on a liquid nitrogen cooled substrate at 80 K would be possible at much higher partial pressures than used here, but this dynamic equilibrium would most likely have a deleterious effect on BLAG. In previous studies with Ar buffers, we found that 20 K was an upper limit for BLAG, with desorption at 35–40 K.