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Clustering in Pb thin films on bromine-passivated Si(1 1 1) surfaces

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Abstract

Thin Pb films, deposited on clean Si surfaces at room temperature (RT), show spectral broadening in ion backscattering spectra due to clustering of Pb, when annealed [Nucl. Instr. and Meth. B 190 (2002) 641]. In order to study the dynamics of clustering on bromine-passivated Si(1 1 1) substrates, Pb thin films (∼1–3 nm) were deposited from a Knudsen cell under ultrahigh vacuum conditions. Each film was deposited at RT and subsequently annealed at 100, 150 and 260 °C for about 4 h. Five Rutherford backscattering spectrometry (RBS) measurements were made at different time intervals for each annealing . Analysis of RBS spectra of as-deposited and annealed Pb films, does not show any significant spectral broadening in annealed Pb films. However, island formation has been confirmed by transmission electron microscopy on a 100 °C-annealed sample. Clustering has apparently occurred in the as-deposited film due to lower surface free energy of the passivated substrate and further detectable growth in cluster height has not occurred in annealing.

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1. Introduction

Scattering and energy loss phenomena in ion–solid interactions are utilized in surface and thin film analysis. In an area of tremendous recent interest – namely, growth of self-assembled nanostructures – clustering phenomena on surfaces are important. Ion scattering techniques can provide valuable information on average cluster height, exponent of growth power law, activation energy of clustering, etc.

Clustering on surfaces usually occurs in thin film growth on solid substrates. Cluster formation is often thermodynamically favoured over random adatom distributions or uniform layer growth and thereby influences the film/substrate interface quality. The kinetics of clustering depend on surface processes, such as surface diffusion, adsorption and desorption. Clustering phenomena in turn influence the interpretation of these parameters [1]. The process of clustering is an important example of macroscopic nonequilibrium thermodynamics where clustering represents a surface phase transition and phase separation [2]. The presence of clusters or islands and their size distribution are usually determined by microscopic

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techniques. However, the study of dynamics of cluster formation often requires additional techniques. Ion scattering is a useful technique to study clustering dynamics. Zinke-Allmang, Feldman and Grabow have recently reviewed the theoretical and experimental aspects of clustering on surfaces [3].

Clustering dynamics is characterized by a measurement of (a) the time dependence of the critical cluster size, $r_c(t)$, and (b) the cluster size distribution. The first dependence tests self similarity and establishes the exponent of growth power law. The latter allows comparison with predicted cluster size distribution. A direct measurement of the average cluster size can be obtained with Rutherford backscatttering spectrometry (RBS) using H or He ion beams of 0.5–2 MeV energies. The shape of energy spectrum reflects the cluster shape and size distribution. The growth exponent can be determined from time-dependent RBS measurements. When these measurements are performed at different sample temperatures, activation energy for clustering can be obtained from the variation of growth rate.

In our earlier experiment on Pb deposition on atomically clean Si(1 1 1) surfaces followed by annealing, we observed broadening of the RBS spectrum due to Pb – indicative of clustering of Pb on the Si surface. Cluster formation was confirmed by atomic force microscopy (AFM) [4]. We intend to study the dynamics of clustering in this system. As the clustering is also influenced by the surface free energy of the substrate, before studying the details of clustering process on atomically clean Si(1 1 1) surfaces, it would be worthwhile to study the clustering on a passivated Si(1 1 1) surface, which has lower surface free energy compared to atomically clean Si(1 1 1) surface. Here we present our studies on chemically bromine-passivated Si(1 1 1) surfaces (hereafter referred to Br–Si(1 1 1)).

2. Experimental

The ion scattering experimental facility consists of an ultrahigh vacuum (UHV) chamber equipped with standard surface analytical techniques like low energy electron diffraction (LEED) and Auger electron spectrometry (AES) (with a four-grid LEED equipment), sputter cleaning of the sample with Ar^+ ions, thin film deposition using Knudsen cells and a six-axis goniometer for RBS/channeling experiments. The goniometer has e-beam sample heating arrangement. In situ ion scattering experiments can be performed on ultrathin films grown under UHV condition. The UHV chamber is connected to a beam line of a 3 MV Pelletron accelerator through a differential pumping arrangement. The pressure achieved in the UHV chamber is 5×10^{-10} mbar. The method of preparation of Br–Si(1 1 1) samples was described elsewhere [5]. Br–Si(1 1 1) samples (P doped with resistivity 10–20 Ω cm) were loaded first in a load lock chamber and transferred one by one to the goniometer in the UHV chamber containing one Knudsen cell for Pb deposition. Pb (5N purity) films were deposited onto the Br–Si(1 1 1) substrates at room temperature (RT). The rate of deposition was determined by calibrating Pb thickness using RBS measurements. The Pb/Br–Si(1 1 1) samples were annealed at 100, 150 and 260 °C. During each annealing RBS measurements were made in order to determine the height of clusters on the surface. RBS measurements were made on as-deposited and annealed samples using a 1 MeV He^+ ion beam. Five RBS spectra were collected as a function of annealing time for each annealing temperature. Morphology of the annealed samples were studied ex situ by transmission electron microscopy (TEM).

3. Results and discussion

RBS results of different measurements are shown in Fig. 1. The bottom spectrum is from an as-deposited sample. From the simulated spectrum the thickness (1.20 nm) of the Pb layer was obtained. For each annealing temperature five RBS spectra were collected with a given time interval to determine the cluster height growth rate from these spectra. The last spectrum obtained in this sequence is shown in Fig. 1 for each annealing temperature (100 °C (266 min), 150 °C (265 min), 260 °C (294 min)). We do not observe any significant change in the spectra compared to the

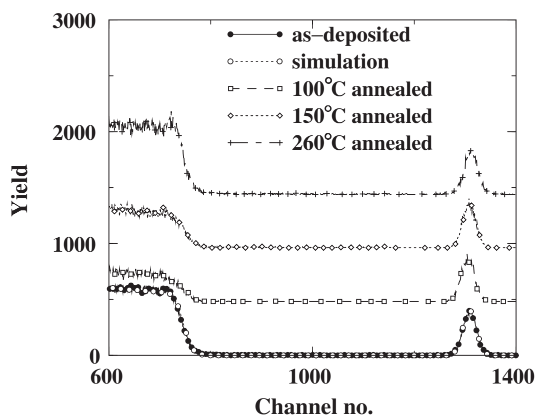

Fig. 1. RBS spectra from an as-deposited Pb-layer on a Br–Si(1 1 1) surface and from similar samples annealed at 100, 150 and 260 °C. Equivalent thickness of the Pb layer is obtained from simulations. The bottom and the top spectra correspond to the same sample before and after annealing.

corresponding as-deposited samples. This is seen from a comparison of the bottom and the top spectra (Fig. 1), which correspond to the same sample before and after annealing. The Pb film thicknesses were somewhat different for different as-deposited films. At the end of about 4.5 h annealing we notice that some Pb desorption has occurred for the 150 °C and 260 °C-annealed samples (see Table 1). RBS results do not show any significant broadening of the part of the spectrum due to scattering from Pb. All the RBS spectra are similar to those for the as-deposited samples. This indicates that clusters probably have already formed on the as-deposited sample and the average cluster size remained more or less constant during thermal treatment. On an atomically clean Si(1 1 1) surface we observed broadening of the RBS spectrum and cluster formation for annealing at 300 °C for 30 min [4]. That is why we have undertaken studies at temperatures below 300 °C. Apparently for Pb deposition on Br–Si(1 1 1) surfaces, clusters are formed in the as-deposited sample. In order to investigate this aspect we performed TEM studies. At the end of RBS experiments, we were left with all annealed samples. We performed TEM studies on the sample annealed at the lowest temperature (100 °C). A plan view TEM micrograph from this sample is shown in Fig. 2, where clusters are seen.

Table 1
Equivalent thickness of the Pb layer before and after annealing ($1\ \text{nm} \equiv 3.3 \times 10^{15}$ Pb atoms/cm^2)

As-deposited film thickness (nm)	Annealing temperature (°C)	Annealing time (min)	Annealed film thickness (nm)
1.63	100	266	1.63
2.76	150	265	2.20
1.20	260	294	1.10

Typical uncertainty in the Pb coverage is ∼3%.

For heteroepitaxial growth the growth morphology is determined by the substrate surface free energy (σ_s), film surface free energy (σ_f) and the interface energy (σ_i). For heteroepitaxial growth the lattice mismatch between the layer and the substrate also influences the growth mode [6]. When $\sigma_s \ll \sigma_f$ cluster formation is favoured. In the present case σ_s has been lowered by surface passivation compared to the atomically clean surface ($\sigma_s^p < \sigma_s^c$). This possibly causes cluster growth directly in the as-deposited layer, even without any heat treatment.

For Ge growth in RT deposition on Br–Si(1 1 1) surfaces, cluster formation was observed. For a 60 nm thick film a compact nanostructural layer and isolated islands on the layer were observed in the as-deposited sample at RT [7]. From annealing experiments up to 500 °C and X-ray reflectivity measurements we determined the activation energy for clustering [8]. On polymer-coated Si surfaces, where the surface free energy is much lower

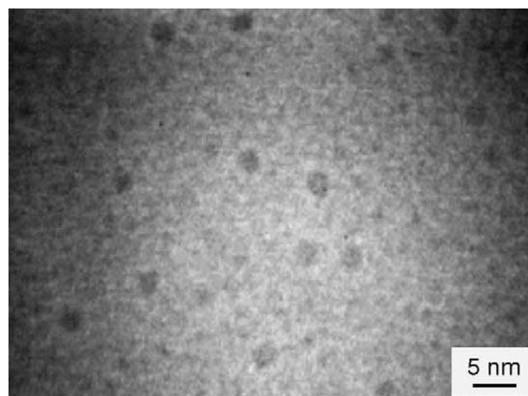

Fig. 2. Plan-view TEM image of a 100 °C-annealed thin Pb layer on Br–Si(1 1 1). Formation of small clusters are seen in the micrograph.

compared to a clean Si surface, deposition of 5 nm Ge at RT produced nanostructural islands – dots and wires [9]. In the present case for a thin Pb layer (∼1–3 nm) stable clusters have apparently formed in RT deposition on Br–Si(1 1 1) surfaces. The cluster height has not grown (beyond RBS depth resolution) further upon annealing. Thus the present system has not allowed us to study the dynamics of cluster formation.

4. Conclusions

We have studied the clustering phenomenon in Pb deposition on bromine-passivated Si(1 1 1) surfaces. Apparently the reduction of Si surface free energy due to passivation gives rise to Pb cluster formation directly in the as-deposited layer at RT. Post-deposition annealing apparently does not increase the average cluster size beyond the RBS depth resolution and thus does not allow the study of clustering dynamics. Growth on the passivated substrate directly leads to island growth.

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