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Energetics of Ge nucleation on SiO_2 and implications for selective epitaxial growth

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ABSTRACT

We have measured the time evolution of Ge nucleation density on SiO_2 over a temperature range of 673–973 K and deposition rates from 5.1×10^{13} atoms/cm^2 s (5 ML/min) to 6.9×10^{14} atoms/cm^2 s (65 ML/min) during molecular beam epitaxy. The governing equations from mean-field theory that describe surface energetics and saturation nucleation density are used to determine the size and binding energy of the critical Ge nucleus and the activation energy for Ge surface diffusion on SiO_2. The critical nucleus size is found to be a single Ge atom over substrate temperatures from 673 to 773 K, whereas a three-atom nucleus is found to be the critical size over substrate temperatures from 773 to 973 K. We have previously reported 0.44 ± 0.03 eV for the Ge desorption activation energy from SiO_2. This value, in conjunction with the saturation nucleation density as a function of substrate temperature, is used to determine that the activation energy for surface diffusion is 0.24 ± 0.05 eV, and the binding energy of the three-atom nucleus is 3.7 ± 0.1 eV. The values of the activation energy for desorption and surface diffusion are in good agreement with previous experiments of metals and semiconductors on insulating substrates. The small desorption and surface diffusion activation barriers predict that selective growth occurring on window-patterned samples is by direct impingement of Ge onto Si and ready desorption of Ge from SiO_2. This prediction is confirmed by the small integral condensation coefficient for Ge on SiO_2 and two key observations of nucleation behavior on the window-patterned samples. The first observation is the lack of nucleation exclusion zones around the windows, and second is the independence of the random Ge nucleation density on patterned versus unpatterned oxide surfaces. We also present the Ge nucleation density as a function of substrate temperature and deposition rate to demarcate selective growth conditions for Ge on Si with a window-patterned SiO_2 mask.

1. Introduction

Selective epitaxial growth (SEG) of Ge and SiGe has become increasingly important in a variety of advanced applications, including high-speed heterojunction bipolar transistors [1–3] and metal oxide field-effect transistors [4–7]. Other applications include ordered arrays of quantum dots [8–12] for photodetectors [13] and quantum cellular automata [14]. The SEG technique has also been used in conjunction with epitaxial lateral overgrowth [15–17] to define areas of low-defect-density films lattice-mismatched to the underlying substrate. This latter technique, in particular, allows integration of III–V compound semiconductor films with Si, provided that the III–V material (e.g., GaAs) is closely lattice matched to Ge. The III–V integration on Si in turn lends itself to a variety of useful applications, such as multijunction solar cells and high electron mobility transistors.

The SEG methods require patterning of holes or trenches in a dielectric mask layer that typically consists of SiO_2 or Si_3N_4. For successful SEG, random nucleation on the mask must be prevented. Thus, it is important to determine the mechanisms and energetics of nucleation on the mask responsible for optimal selectivity. The nucleation energetics can be extracted by applying atomistic nucleation theory to measurements of island densities on the mask.

Nucleation theory of thin films deposited from the vapor has a long history and originated from metal nucleation studies, eventually leading to semiconductors. Since the development of atomistic nucleation theory by Walton [18] and the rate equation approach by Zinsmeister and others [19–21], a large body of research has been done to test the predictions of the theory. Early work was focused on Au deposition onto alkali halide substrates [22–24]. While providing qualitative confirmation of the theory, early nucleation studies on alkali halide substrates were complicated by the formation of defects on the substrate caused by stray electrons emitted from the deposition source. These defects caused additional nucleation to occur on the substrate during the deposition [25]. More recently, Schmidt et al. [26] studied the nucleation of several metals on amorphous SiO_2 films and found that their nucleation behavior agreed with nucleation theory. In general however, metal nucleation on insulating substrates appears to be dominated by surface defects, especially at low deposition

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temperatures [27–29]. Following the metal–insulator studies, metal–metal and metal–semiconductor systems were studied and found to differ in nucleation energetics and behavior from insulating substrates [30].

These early nucleation studies are examples of Volmer–Weber or Stranski Krastanov growth, during which nucleation densities are measured by either scanning electron microscopy (SEM) or transmission electron microscopy. With the advent of scanning tunneling microscopy (STM), nucleation and island growth are studied at the atomic level with sub-monolayer sensitivity, and much insight is gained into the fundamental processes of 2D atomic motion on surfaces. The use of STM provides the opportunity to test nucleation theory at the atomic level. Explicit measurement of critical nucleus sizes and the flux dependence of the stable island density quantitatively validated the rate equation approach to modeling nucleation of thin films [31–36]. Complementing the STM work, Monte Carlo simulations have also confirmed that the rate equation approach is an accurately quantitative description of the nucleation process [37]. Although measurements using low-temperature STM are more precise than those inferred from SEM using nucleation theory, the STM cannot be used on insulating substrates. Thus, we use SEM in this study to measure nucleation densities of Ge on SiO_2.

In previous studies of metal and semiconductor growth on insulators, island growth is generally observed due to low surface energy of the insulators, and this is also the case for Ge–SiO_2 at typical growth temperatures (673–923 K) used in our experiments. In addition, these systems are characterized by small adsorption and surface diffusion energies. For example, for Ag on SiO_2, Poppa [38] estimates the desorption energy as 0.52–0.43 eV. Specifically for Ge on SiO_2, we reported 0.44 ± 0.03 eV [39] for an experimentally measured desorption activation energy of Ge from SiO_2. In the present study, we extend the measurement of Ge nucleation on SiO_2 over a much broader range of temperatures and deposition rates and extract the critical nucleus size, cluster binding energy, and surface diffusion energy of Ge on SiO_2 from the rate equation approach to nucleation.

2. Experimental methods

Germanium is grown by molecular beam epitaxy (MBE). The base pressure of our MBE chamber is approximately 5×10^{-10} Torr, and the chamber is equipped with an entrance load-lock for sample introduction. We use a dual filament effusion cell with a manually operated shutter as a Ge source. The effusion cell temperature ranges from 1273 to 1473 K. Germanium flux is quantified by measuring the Ge film thickness on Si substrate held at room temperature, assuming that 100% of Ge adsorbs onto Si and subsequently onto Ge. After opening the shutter, the time of deposition and effusion cell temperature are recorded, and the film thickness is measured from cross-sectional SEM images. The flux is found to be reproducible within ±5% at a given effusion cell temperature. For Ge growth on SiO_2, the sample is heated by a Boralectric Heater (50 mm $w \times 50$ mm l) made by GE Advanced Materials. The temperature of the heater is measured using a K-type thermocouple and verified with a calibrated pyrometer. The two measurements agree to within 8° over the experimental range of 673–973 K.

For SiO_2 sample preparation, Si wafers are first cleaved into narrow strips of 1 cm $w \times 5$ cm l pieces. The Si wafers are doped with boron with a resistivity of 1–10 Ω cm. The cleaved samples are cleaned in a Pirhanna bath consisting of three volumetric parts H_2SO_4 (96 wt%) to one part of H_2O_2 (30 wt%). The samples are subsequently dipped into a buffered oxide etch solution (20 parts 40 wt% NH_4F:1 part 49 wt% HF) diluted in deionized (DI) water by 6:1 volumetric ratio to remove the chemical oxide. The chemical oxidation and etching process is repeated twice. The samples are dried with N_2 and then loaded into a dry oxidation furnace, in which 100 nm of oxide is grown at 1423 K. Before Ge deposition, the samples are again cleaned in Pirhanna and dipped into a dilute HF solution for 10 s. The dilute HF is made by mixing 20 volumetric parts of DI water with one part of 49 wt% electronic grade HF solution. After the HF dip, which removes approximately 1 nm of the thermally grown SiO_2, the samples are rinsed in DI water and dried with N_2 gas. After being loaded into the deposition chamber, the samples are degassed at 873 K for 10 min. The effusion cell is set to the desired temperature and allowed to stabilize for 30 min. The substrate heater is then set to the deposition temperature and allowed to stabilize for 5 min. The shutter is subsequently opened for deposition, while the deposition time is recorded. The pressure in the chamber remains below 1×10^{-8} Torr during the deposition.

After deposition, the Ge nucleation density is counted *ex situ* from SEM images. The microscope is a JEOL 6400F capable of ~10 nm resolution. The samples are sputter coated with 5 nm of Au to prevent charging of the SiO_2 surface during SEM imaging and to enhance the resolution and contrast of Ge islands. Eight images are recorded across the sample in plan-view geometry to provide reliable counting statistics for nucleation densities. The island densities vary by 2–4 times from center to edge of the samples. Sample edges are more prone to variation due to possible contamination from cleaving and sample handling. Thus, we limit our counting to eight locations near the center along the 5-cm strip to minimize edge effects. Fig. 1 shows representative SEM micrographs where the island nucleation density decreases with increasing substrate temperature at a fixed flux of 4.2×10^{14} atoms/cm^2 s (40 ML/min). The islands appear semicircular and are randomly distributed across the surface.

3. Results and discussion

The number of Ge islands nucleated on the SiO_2 is a function of substrate temperature T_{sub}, deposition rate R, and time t. Nucleation density measurements are made over substrate temperatures from 673 to 973 K and deposition rates from 6.9×10^{14} atoms/cm^2 s (65 ML/min) to 5.1×10^{13} atoms/cm^2 s (5 ML/min). Fig. 2 shows the time dependence of the nucleation density at a fixed deposition rate for several substrate temperatures. The time to reach the saturation nucleation density decreases with decreasing substrate temperature and increasing deposition rate. Qualitatively, at low temperatures, a larger number of Ge adsorbates exist on SiO_2 surface to form islands, and therefore a larger overall nucleation density. This in turn is likely to cause the system to reach the saturation density much more quickly than at elevated temperatures.

The saturation nucleation density can be described by the following formula given by Venables et al. [40]:

$$\frac{N}{N_o} \sim \left(\frac{R}{N_o \nu}\right)^p \exp\left[\frac{E_n}{k_B T_{sub}}\right], \tag{1}$$

where N is the saturation island density, N_o is the number of possible adsorption sites on the substrate, ν is a characteristic surface vibration frequency, and k_B is Boltzmann's constant. The exponent p and activation energy E_n depend on whether the islands are 2D or 3D and whether condensation is complete or incomplete [40]. The level of condensation is often categorized into three regimes: extreme incomplete, initially incomplete, and complete [40]. Extreme incomplete condensation is associated with low desorption (E_{des}) and diffusion (E_{diff}) activation barriers. These low activation barriers lead to an extremely short characteristic surface diffusion