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Formation of the wetting layer in Ge/Si(111) studied by STM and XAFS

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Abstract

We have followed by scanning tunneling microscopy (STM) the Stranski–Krastanov (SK) growth of thin Ge films obtained by reactive deposition epitaxy on a Si(111) surface. For Ge thickness smaller than 1.2 ML, STM images show large flat regions (reconstructed 7×7) without protrusions. With increasing thickness Ge-Si 2D islands (reconstructed 5×5) start nucleating, while the Si substrate retains its original 7×7 reconstruction. The islands are flat and have a triangular shape with a lateral size which increases progressively with deposition. We have studied the growth law of the average dimensions of the islands and of the average number of islands per unit surface as a function of coverage. STM images suggest a sizeable process of intermixing at the Ge/Si interface, which has been directly confirmed by XAFS (X-ray absorption fine structure) spectra on Ge/Si(111) samples. We have followed the evolution of the wetting layer up to its completion, both after and during deposition. The appearance of a percolated structure is observed when a critical fraction of the surface (about 70%) is covered.

Keywords: Crystal growth; Intermixing; Random alloy; Percolation; Wetting layer; Lattice strain

1. Introduction

Heteroepitaxial Ge/Si alloys are promising materials for microelectronic [1] and optoelectronic [2] applications. The strain caused by the 4.2% difference in the Ge vs. Si lattice parameters can be advantageous when growing quantum self-organized nanostructures; this is an essential requirement for several novel applications, such as heterojunction bipolar transistors and quantum devices.

The main questions to be pursued are: how the strain leads to island formation and the role of Ge-Si intermixing [1–5]. Besides, it is not yet possible to grow islands of desired size, shape and density: the experimental results available today are still lacking detailed knowledge of the Stranski–Krastanov (SK) growth dynamics, particularly on the atomic scale.

Several studies of the surface properties of the Ge/Si(111) system have been performed using different methods [6–10], suggesting the formation of Ge_xSi_{1-x} alloys due to the strain on the substrate [11–13] or to kinetic effects [14–16].

The application of scanning tunneling microscopy (STM) to measure the in-plane surface lattice strain η_s [17] and the degree of ordering of the resulting alloy has already been undertaken. The observation of the height modulation of the adatoms [18,19] in the 5×5 surface has led to contrasting conclusions on the distribution of the adatoms and on the elemental composition of the wetting layer. Accurate measurements of the in-plane lattice constant of Ge/Si(111) islands show a progressive increase of the interatomic distance as a function of the island height towards that of pure Ge [17]. This relaxation suggests an enrichment in Ge content of the islands up to about 100%. However, so far, no definite conclusions about the true composition, the lattice parameter and the ordering of the wetting layer have been reached.

In the present paper, we study the evolution and formation of the wetting layer from different points of view. X-ray absorption fine structure (XAFS) data allow us to demonstrate the presence of substantial intermixing, as indirectly confirmed by STM images.

2. Experimental

2.1. Growth and nanoscopic characterization

The experiments were performed with a commercial STM (OMICRON VT), in a UHV chamber (base pressure $\sim5\times10^{-11}$ mbar) also containing a LEED-Auger facility and an e-gun evaporator. The Si substrates consisted of p-

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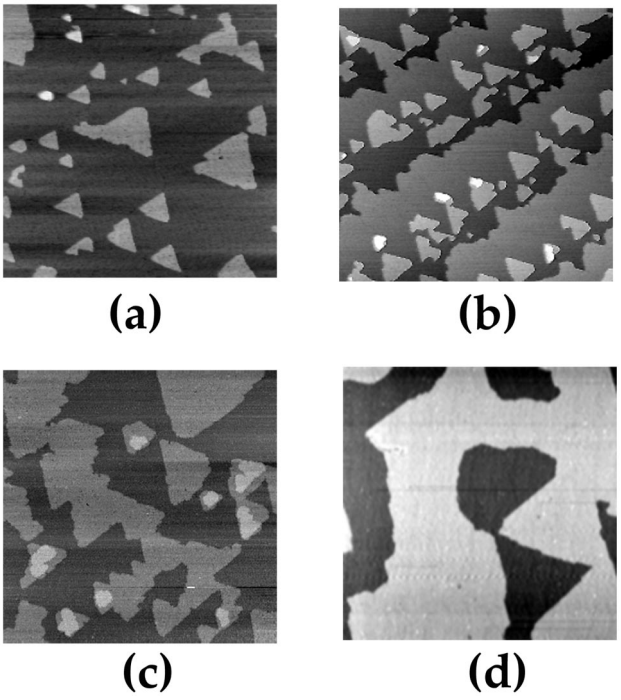

Fig. 1. STM image of a Ge/Si(111) sample; (a) 0.65 ML Ge coverage, $(2700 \times 2700 \times 3)$ Å^3; (b) 1 ML Ge coverage, $(4000 \times 4000 \times 5)$ Å^3; (c) 1.35 ML Ge coverage, $(2000 \times 2000 \times 6)$ Å^3: notice the interaction between the steps and the islands; (d) 2 ML Ge coverage, $(2000 \times 2000 \times 3.6)$ Å^3.

doped Si(111) wafers ($\sim 0.4 \times 1.0$ cm) of resistivity $\rho \approx 0.003\ \Omega$ cm. For each deposition, we started from a reconstructed Si 7×7 surface obtained by repeatedly flashing (for about 40 s) the sample at 1250°C by direct current heating with a current of about 9 A. The temperature of the sample surface was checked by means of an optical pyrometer. Surface reconstruction and cleanliness were monitored by low energy electron diffraction (LEED) and Auger spectroscopy. The deposition of Ge on the Si substrate kept at 500°C was made from a Knudsen cell with low evaporation rates of 0.1–0.3 ML min^{-1}. Each Ge deposition was made on a new Si sample in order to minimize the uncertainties of successive evaporations.

2.2. X-ray absorption fine structure measurements

XAFS spectra at the Ge K-edge were taken at the BM8 'GILDA' CRG beamline of the European Synchrotron Radiation Facility [4] on two different Si(111) samples, on which were deposited, respectively, 10 and 17 A equivalent thickness of Ge; the samples were prepared in the UHV chamber described in Section 2.1 above. Spectra were acquired in two geometries, exploiting the linear polarization of the synchrotron radiation photon beam: with the angle between the electric vector of the photon beam and the normal to the surface either 15 or 75°; these two geometries preferentially probe the structure either perpendicular or parallel to the growth plane, respectively. XAFS spectra were recorded in the fluorescence mode, using a seven element hyper-pure Ge detector.

Table 1
Number of islands (N) and fraction of covered surface (S/S_0) as a function of deposited thickness θ in the interval 2.5–4.5 Å (0.65–1.35 ML)

N ($\times 10^{-6}$)	S/S_0	θ (Å)
4.02 ± 0.09	0.25 ± 0.08	2.5 ± 0.1
2.51 ± 0.97	0.33 ± 0.05	3.0 ± 0.1
1.35 ± 0.53	0.42 ± 0.04	4.5 ± 0.1

3. Results

3.1. Growth law of the wetting layer

Our STM images (Fig. 1a–d) are helpful in understanding the process of formation of the wetting layer. As can be recalled from [3], when a few ML (0.5/2)of Ge are deposited on the surface, 2D Ge islands start to grow on the Si substrate and have a triangular shape with a lateral size which increases progressively with deposition. If we reasonably assume that all the Ge deposited contributes to the growth of the wetting layer, one would expect that $S \propto \theta$ (here S is the fraction of surface covered with Ge, while θ is the total Ge deposited), as can be actually inferred from the data reported in Table 1. However, a log–log plot of N vs. θ yields a linear behavior, meaning that the average number of islands per unit surface, N, scales as a power of total coverage, θ: $\langle N(\theta)\rangle\ \mu\,\theta\mu$, we find $\mu = -1.80 \pm 0.80$; (see Table 1 and Fig. 2). Since $\langle N(\theta)\rangle\ \mu S/\langle r\rangle^2$, this would naturally lead to a growth law of the type: $\langle r(\theta)\rangle \mu\,\theta^{1/z}$ [20,21],with a critical index $z = 0.70 \pm 0.20$; remarkable the correlation coefficient is 0.99, but unfortunately, we only have three experimental points which highlight this behaviour. Here, r denotes the average dimension of the islands as a function of coverage. This could seem rather puzzling at first thought; however, we note that, in some cases, like that

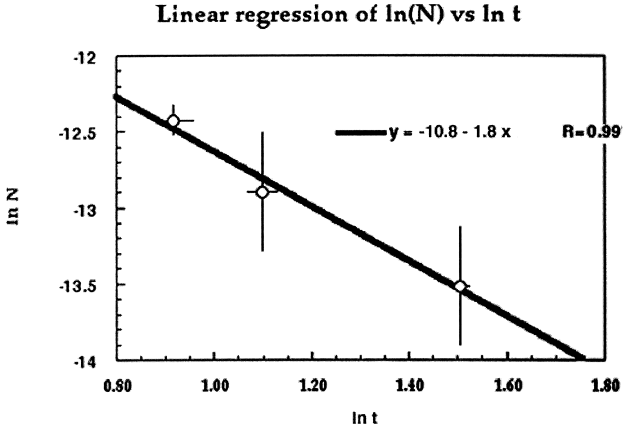

Fig. 2. Linear regression of ln(N) vs. ln t; here we assume θ proportional to t since deposition was performed at constant flux.

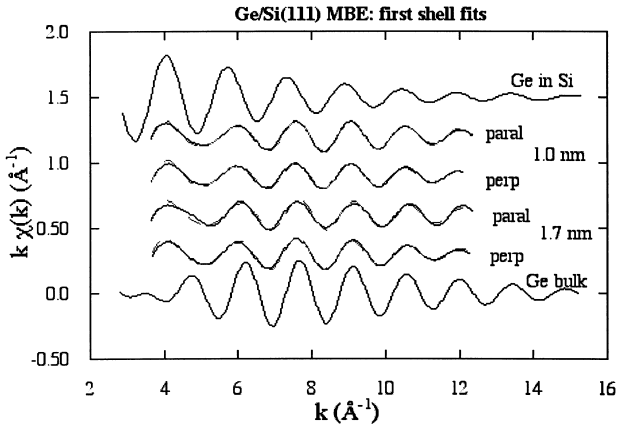

Fig. 3. XAFS spectra and first shell fits for the two Ge/Si(111) samples, in perpendicular and parallel geometries.

illustrated in Fig. 1b, the formation of steps due to lattice strain begins to affect the process of completion of the wetting layer, making it difficult to count properly the average number of islands.

We are planning further experiments in which we would like to control the dimensions of the steps, with the purpose of determining the correct growth law for the formation of the wetting layer.

As coverage increases (2–4 ML) the islands start to impinge on each other (Fig. 1c), forming larger islands each made of several smaller triangular islands. When about 70% ($S/S_0 = (0.69 \pm 0.05)$) of the surface is covered with Ge, a percolated structure appears (Fig. 1d); this is consistent with the results reported in Ref. [22] for percolation on the continuum. Further experiments should enable us to measure more precisely the critical percolation threshold.

3.2. Intermixing

An estimation of the average intermixing and of the local distortion is obtained by the XAFS measurements. XAFS data were analyzed using standard procedures, by Fourier-filtering techniques [23]. In Fig. 3 we show the filtered contribution from the first shell around Ge for the samples and for standards of pure Ge and of a Ge impurity in crystalline Si. The signals relative to the samples were fitted using experimental phase shifts to obtain the local structural parameters. In the fitting the total coordination number was fixed to 4. No difference in the perpendicular or parallel polarization was detected.

For Ge-Si bonds we find a coordination number of $N_{\text{Ge-Si}} = 2.0 \pm 0.3$.

The reported $N_{\text{Ge-Si}}$ measure the average coordination of Ge atoms in the alloy. Several reports in the literature claim that both amorphous [24,25] and crystalline [13,26] Ge-Si alloys are random alloys, which means that there is no preference for or against heteroatomic bonding; this is also consistent with the very similar electronegativities and the small difference in covalent radius of the constituent atoms. It is, therefore, reasonable to use the coordination numbers as a measurement of average composition; for our two samples we find an average composition of $Ge_{0.5}Si_{0.5}$ [2]; it must be stressed that these are average values, therefore neglecting any gradients which might exist, but to which the XAFS technique is not sensitive.

The Ge-Ge and Ge-Si bond lengths were found to be 2.44 ± 0.1 and 2.41 ± 0.01 Å, in good agreement with the values reported in a recent comprehensive study of crystalline Ge-Si alloys by Aubry et al. [27].

In order to compare surface and bulk Ge-Si intermixing, STM and CITS data have been compared with XAFS results. In Fig. 4 we present the plot profiles taken on filled-state topographic images. The CITS data, reported in Ref. [19], show similar features. There are noticeable

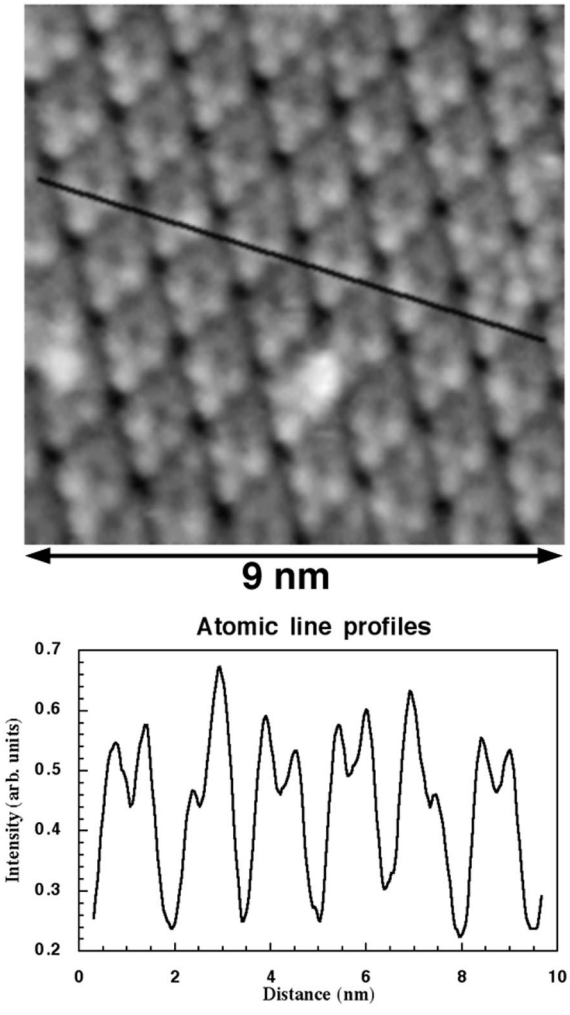

Fig. 4. Topographic filled-state image of the 5×5 reconstructed Ge/Si(111) surface, and atomic line profiles corresponding to the continuous line traced on the image.

differences in the height of subsequent peaks; high and low peaks are distributed randomly on the 5×5 cell. This could be explained both with a random occupancy (50%) by Si and Ge of the topmost sites at the surface, or with a full Ge occupancy, where the modulation can be caused by the atoms underneath [3].

Due to high diffusion of Si in Ge we are in favor of a model where the Si concentration in the wetting layer is nearly constant, and the topmost layer is randomly occupied.

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