Kinetics of In growth on Si(100)2×1 surface at low coverage – STM study

Ivan Ošťadal, Jakub Javorský, Pavel Kocán, Pavel Sobotík and Martin Setvín
Department of Surface and Plasma Science, Faculty of Mathematics and Physics, Charles University in Prague, V Holešovičkách 2, 182 00 Prague 8, Czech Republic
E-mail: ivan.ostadal@mff.cuni.cz

Abstract. Scanning tunneling microscopy (STM) was used for studying nucleation and growth of 1-dimensional indium islands (chains) at coverage below 0.5 ML on the reconstructed Si(100)2×1 surface at room temperature (RT). In-vivo measurements – direct observations of growth during deposition – provided data on growth kinetics and showed a substantial role of C-defects at adsorption of metal atoms. Density of the metal chains and distribution of the chain lengths were obtained for various amounts of deposited indium. The length of the indium chains was specified with atomic accuracy. The real time observations showed that surface mobility of indium atoms at RT is probably not entirely restricted by the "forbidden zones" accepted in previous growth models.

1. Introduction
Sub-monolayer growth of the group III metals (Al, Ga, In) on the reconstructed surface Si(100)2×1 results in 1-dimensional chains of metal atoms. The scanning tunneling microscopy (STM) considerably contributed to revealing important structural and electronic properties of the metal chains. The indium chains grow perpendicularly to the dimer rows on the silicon reconstructed surface and are composed of metal dimers parallel to the Si dimers [1, 2] – similarly to the other group III metals. The growth was explained as the surface polymerization reaction [3]. Diffusing metal atoms preferentially adsorb at the ends of the metal chains. The chains nucleate at the surface steps and on terraces the nucleation was observed almost exclusively on C-type defects [4, 5, 10]. The C-defects are interpreted as dissociated molecules H2O adsorbed on Si dimers [7, 8]. Real time STM observations of metal adsorption and growth during deposition (in-vivo technique [5]) provided detailed data on growth kinetics. Decay of indium chains during growth at room temperature (RT) plays an important role [4, 5]. In our previous study [5] we dealt with stability of the indium chains at RT and a possible influence of the STM tip. Here we report data on growing the indium chains at RT obtained both by STM in-vivo experiments and by standard STM in-situ observations of layers after deposition.

2. Experimental
A non-commercial STM system was used in experiments performed under ultra-high vacuum conditions (base pressure < 3 × 10−9 Pa). Si(100) samples were cut from the Sb doped silicon wafer (resistivity ≤ 0.014 Ωcm). The 2×1 reconstruction was prepared by repeated flashing the
Figure 1. Sequence of images taken during deposition (tip voltage +2 V, tunneling current 0.3 nA). The C-type defects are marked by circles. (a)– surface before deposition, the inset shows a form of the C-defect. Arrows in (c) and (d) indicate the growth direction of the chains. (e)– a chain ”kink” near the C-defect. The bright ”flags” in (f) indicate chain ends terminated by a single atom (see text). The images were taken after 24 min (b), 27 min (c), 30 min (d), 36 min (e) and 53 min (f) from starting deposition. Image size: 13×16 nm².

samples to 1200°C for ≈ 20 s (at pressure < 5 × 10⁻⁸ Pa). Electrochemically etched tungsten tips were used. A miniature tungsten wire evaporator was used for depositing indium. An atomic beam was focused on the scanned area by means of three Mo diaphragms – to suppress thermal radiation and protect a scanner from evaporated metal. Deposition rate was ≈ 10⁻⁴ ML/s, 1 ML = 6.78 × 10¹⁴ atoms/cm². The rate was estimated from STM images. The scanning speed was ≈ 300 nm/s; rate of STM imaging: ≈ 1 image/min; size of images taken during the in-vivo measurements: 40 × 40 nm².

3. Results and discussion

The surface mobility of free indium adatoms at RT is too high – they can be recorded by STM only after reaching stable positions. The Fig. 1 shows a set of images chosen from a sequence obtained at one in-vivo experiment. Positions of C-defects on the clean Si(100) 2×1 surface before starting depositions are marked by the circles – image (a). The inset represents filled state imaging of the most frequent form of the C-defect. The following images demonstrate adsorption of In atoms at the C-defects and growth of In chains. Chain terminations are fixed at positions of the defects, the growth direction is given by orientation of the C-defects on the surface – see the arrows in (c) and (d) images. The ”kink” on a chain growing in proximity of the C-defect is visible on the image (e). Our results reported in [5] show that the chain terminations at C-defects are ”dark” on filled state images. The growing ends are imaged ”normally” when terminated by a dimer or like bright spots when a single metal atom terminates the chain. The single atom terminations are indicated by bright ”flags” visible on the image (f) – the flags are image artefacts due to insufficiently fast response of electronic controlling tip-sample distance in the constant current mode (scan direction is right to left).

The Fig. 2–4 contain growth characteristics obtained from the STM images taken at in-vivo experiments and measurements on layers of various coverage below 0.2 ML prepared before STM observation – relaxed layers. Only the nucleation on large terraces was examined. The surface is saturated at 0.5 ML of deposited In (structure In(2×2) at perfect arrangement). The mean chain density per site (normalized to all adsorption sites) increases with coverage during the growth observed in-vivo (Fig. 2). The data corresponding to the relaxed structures fluctuate around a constant value. The difference in the characteristics can be explained by the presence of the C-defects and preferential nucleation on them. The duration of experiments and small distance (40 mm) of the evaporator from the sample result in increasing density of C-defects – nucleation sites – as was observed in the in-vivo experiments. The standard, one order faster deposition from a distant source practically does not change surface concentration of the C-defects and the number of grown chains. The average length of the indium chains increases with coverage (Fig. 3) and saturates for the in-vivo data at a coverage of 0.25 ML. In case of the
Figure 2. Density of In chains versus coverage obtained at various experiments and RT. The relaxed layers were deposited at rates from $10^{-3}$ to $10^{-2}$ ML/s.

Figure 3. Average chain length (in atoms) saturates at a coverage of 0.25 ML.

Figure 4. Scaled chain size distributions obtained from data measured on two deposited layers of various coverage and during one in-vivo experiment. The in-vivo data represent growth stages up to a coverage of 0.37 ML ($s$–chain length; $<s>$–average chain length; $N_S$–chain density per site; $\Theta$–coverage in ML; $\Theta/<s>$–mean chain density per site).

relaxed layers the increase of the average length is much higher – due to the smaller number of chains nucleated at C-defects. The diagram on Fig. 4 presents scaled chain length distributions obtained for two layers with coverages of 0.04 and 0.08 ML. The third characteristic contains data from images of the whole sequence taken at the in-vivo experiment with a deposition rate $6 \times 10^{-5}$ ML/s up to a coverage of 0.37 ML. The large dispersion of the data for ”short chains” results from statistically insufficient data sets. The in-vivo data agree with those reported for Ga in [9] as an example of monotonically decreasing island size distribution for all coverages. Statistical uncertainty of data plotted in Fig. 4 does not allow decision whether fine structure of the plot – especially in case of in-vivo data – may contain relevant information.

The character of low coverage growth of the group III metals – separation of adjacent chains by a minimum distance $2a$ (where $a$ is the distance between two adjacent Si dimers) and metal adatom bonding to chains only at the end sites – support a concept of sites blocked for adsorption of diffusing adatoms and implementation of such ”forbidden zones” along metal chains into a growth model [9]. Metal adatoms can diffuse along the restricted area only, crossing it or even hopping across a chain is not allowed. We tested probability of such an event using real time STM observations of a surface area surrounded by forbidden zones around indium chains – see Fig. 5. The area consists of two unoccupied adjacent gaps of different lengths which both terminate at a defect (stable termination) – on the right hand side. On the opposite side the gaps (of various length) are closed by terminations of two indium chains. The bright spot on
the image (a) indicates the chain termination by a single In atom. The number of empty sites (which can be occupied by In adatoms) contained in the closed area is indicated on each image. In image (a) the total number of empty sites is $7 + (2 \times 8) = 23$. Repeated scanning of the area shows that In atoms detach/attach from/to the chain ends. A number of empty sites fluctuates during the observation: 22 (b)-(d), 29 (e), 23 (f), 22 (g) and 26 (h). The images (a)–(h) are details cut from a larger scanned area – see (i). Investigation of the whole images showed that indium atoms disappear and appear again in the permanently closed ”basin”. We can almost exclude ”invisible” mobile indium atom(s) in the ”basin” and no effect of STM tip manipulation was observed. It supports the fact that at RT and higher coverage the In adatoms can probably migrate in close proximity of metal chains or even across them.

4. Conclusions

STM experiments in-vivo revealed important features of indium growth on Si(001)2×1 surface. Indium atoms nucleate preferentially on C-type defects, a chain termination at the defect is stable. The real time STM measurements show that surface mobility of indium atoms at RT is not probably entirely restricted by the ”forbidden zones” along metal chains.

Acknowledgments

The work is a part of the research plan MSM 002160834 that is financed by the Ministry of Education of the Czech Republic and partly was supported by the projects GACR 202/06/49, GAUK 225/2006/B, GAUK 227/2006/B and GAUK 100907/2007.

References

[1] Evans M M R and Nogami J 1999 Phys. Rev. B 59 7644
[2] Dong Z C, Yakabe T, Fujita D, Jiang Q and Nejo H 1997 Surf. Sci. 380 23
[3] Brooks G, Kelly P and Car R 1993, Phys. Rev. Lett. 70 2786
[4] Kocán P, Sobotík P and Oštádal I 2006 Phys. Rev. B 74 037401
[5] Kocán P, Sobotík P, Oštádal I, Javorský J and Setvín M 2007 Surf. Sci. 601 4506
[6] Albao M A, Evans M M R, Nogami J, Zorn D, Gordon M S and Evans J W 2006 Phys. Rev. B 74 037402
[7] Okano S and Oshiyama 2004 Surf. Sci. 554 272
[8] Hossain M Z, Yamashita Y, Mukai K and Yoshinobu J 2003 Phys. Rev. B 67 153307
[9] Albao M A, Evans M M R, Nogami J, Zorn D, Gordon M S and Evans J W 2005 Phys. Rev. B 72 035426
[10] Albao M A, Evans M M R, Nogami J, Zorn D, Gordon M S and Evans J W 2006 Phys. Rev. B 74 037402