The influence of anisotropic diffusion on Ag nanowire formation

2009 J. Phys.: Condens. Matter 21 314023

(http://iopscience.iop.org/0953-8984/21/31/314023)

J. Phys.: Condens. Matter **21** (2009) 314023 (4pp) doi:10.1088/0953-8984/21/31/314023

The influence of anisotropic diffusion on Ag nanowire formation

D Wall[1], S Sindermann[1], K R Roos[2], M Horn-von Hoegen[1] and F-J Meyer zu Heringdorf[1]

[1] Department of Physics and Center for Nanointegration Duisburg-Essen (CeNIDE), Universität Duisburg-Essen, D-47057 Duisburg, Germany
[2] Department of Physics, Bradley University, Peoria, IL 61625, USA

E-mail: dirk.wall@uni-due.de and meyerzh@uni-due.de

Received 18 December 2008, in final form 6 March 2009
Published 7 July 2009
Online at stacks.iop.org/JPhysCM/21/314023

Abstract
Photoemission electron microscopy is used to study the growth of single-crystalline silver nanowires on flat and vicinal Si(001) substrates. The growth experiments were performed at various temperatures and showed a temperature dependence of nanowire formation. The nanowires on Si(001) are evenly distributed in the [110] and [1$\bar{1}$0] directions on the surface, whereas on a 4° vicinal surface the wires grow only along the steps, in the [1$\bar{1}$0] direction. This change in wire distribution is attributed to the increasing diffusion anisotropy as the vicinality of the substrate increases.

1. Introduction

Nanowires have attracted significant attention during recent years. With shrinking electronic devices, the ratio of surface to volume increases and size-dependent material properties dominate the behavior. For example, single-crystalline nanowires compared to polycrystalline nanowires show reversed electromigration behavior [1]. In order to control the growth of self-organized single-crystalline nanowires, it is necessary to understand at which sites wires nucleate and in which direction the wires grow.

The latter aspect will be addressed in the present work for Ag nanowires on well-oriented and vicinal Si(001) substrates. Upon deposition of Ag on Si(001), silver islands form on an Ag-induced (3 × 2) [2] reconstruction. These islands are strained due to a lattice mismatch. Simulations [3] predict a transformation of initially symmetrical islands into wires for strained Stranski–Krastanow growth. During our growth experiments, we observed [4] shape transitions of Ag islands similar to the simulation results, i.e. a strain-driven shape transformation. However, other groups have called the numerical value for the stress of 6% [3] into question, and reported lattice mismatch strains below 0.5% for the same system and similar growth temperatures [5–7]. Nevertheless, the shape transformation does not necessarily depend on a stress of 6% and should qualitatively still be valid for the observed lower stress. Recently, it was observed that on vicinal Si(001) surfaces significant diffusion anisotropy exists, which might also favor wire formation [8]. In the present work, we combine a statistical analysis of the wire formation with the data for diffusion anisotropy, adding another piece of vital information on the way to a full understanding of the different influences on the wire formation.

2. Methods

The experiments were performed in an ultra-high vacuum (UHV) low energy electron microscope (LEEM) [9]. Well-oriented as well as 0.2°, 0.8°, 1°, 2° and 4° vicinal (in the [110] direction) Si(001) substrates were cleaned by standard flash annealing after degassing at 600 °C in UHV for several hours. Ag was evaporated from an e-beam-heated tantalum crucible. The Ag deposition took place at elevated substrate temperatures (500–750 °C) and was monitored *in situ* with photoemission electron microscopy (PEEM) or LEEM. The PEEM experiments were carried out using an Hg discharge lamp for illumination. The sample temperature was measured with an infrared pyrometer. LEEM dark-field contrast [10] was used to analyze the influence of steps on the nanowire formation. To gain statistically significant data on the orientation of the wires, the samples were also analyzed *ex situ* with scanning electron microscopy (SEM).

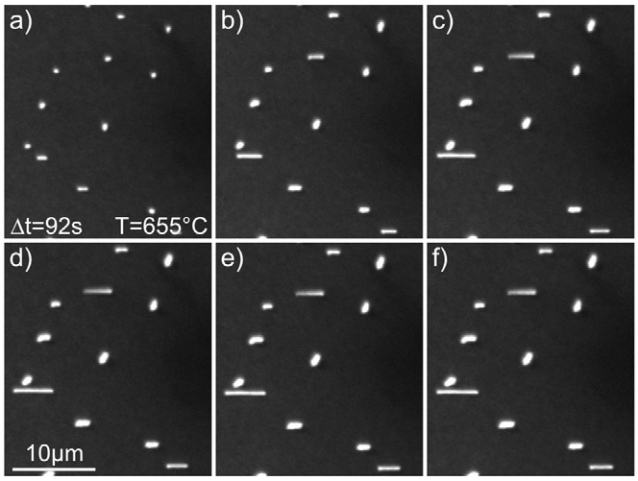

Figure 1. Sequence of PEEM images obtained during growth of Ag islands and nanowires on a Si(001)-4° vicinal surface. (a) Nucleation phase, only compact islands are visible, (b) some islands transform into wires. (c)–(f) The wires grow one-dimensionally while the compact islands grow in a 3D fashion. The scale bar is the same for all images.

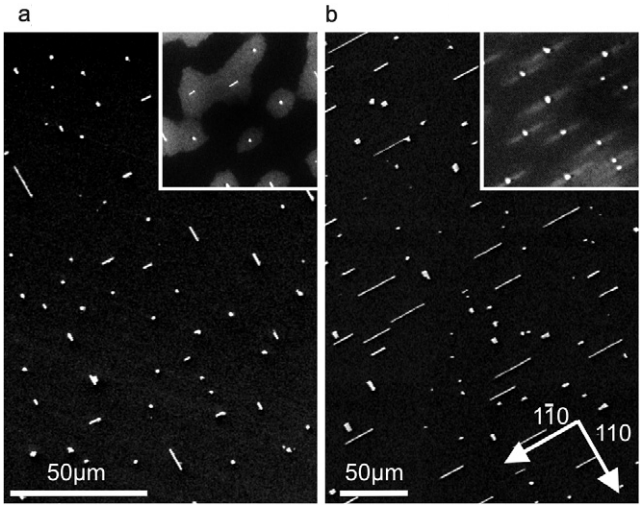

Figure 2. SEM images of typical Ag island and Ag nanowire distributions on (a) Si(001)-0° and (b) Si(001)-4°. The insets show typical diffusion fields [11] that were acquired with PEEM. The scaling and orientation of the insets and the corresponding SEM images is the same.

3. Experimental results

During deposition, the Ag adatom concentration gradually increases, leading to a phase transition from the initial (2 × 1) to the Ag-induced (3 × 2) reconstruction [2]. Once this phase completely covers the surface, 3D crystalline islands and single-crystalline nanowires form atop this intermediate layer. Figure 1 shows an image sequence of a typical growth experiment on a 4° vicinal Si(001) surface. In figure 1(a), all Ag islands have a similar shape and it is impossible to tell which island will eventually turn into a wire. When the islands have reached a certain size (figure 1(b)), some of the islands become elongated. Afterward, the wires grow only in the elongated direction while the islands continue their normal growth (figures 1(c)–(f)). On Si(001), nanowires form in both the [110] and [1$\bar{1}$0] directions (figure 2(a)). In contrast, on the Si(001)-4° vicinal surface, the nanowires form only in one of the two symmetry directions on the surface (figure 2(b)), namely parallel to the double steps. For Ag(001) islands, which are forming above 600 °C [6, 7], the lattice mismatch is identical in the two principal lattice directions and the wires are evenly distributed along the two possible dimer directions. Although the lattice mismatch of an Ag(001) island on an Si(001) substrate will be the same as the lattice mismatch for an Ag(001) island on a vicinal substrate, the distribution of the wires changes significantly. On a 4° vicinal surface, the wires are all aligned to the step edges. We believe this change in the wire distribution to be induced by diffusion anisotropy. In our previous work [11, 12], we established an imaging technique to observe diffusion fields in PEEM. For the imaging of diffusion fields, small Ag islands are deposited on the surface. When the temperature is raised, the islands decay by feeding adatoms onto the surface, which then diffuse over the surrounding area and desorb. As a result, a coverage gradient establishes around each island and different reconstructions are formed, depending on the local coverage. On Si(001), these

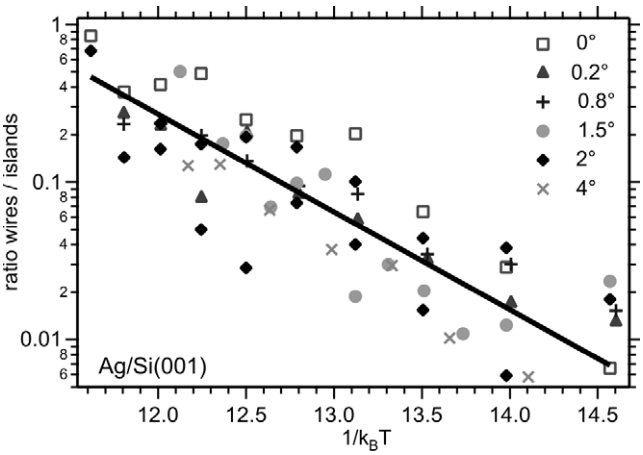

Figure 3. Temperature dependence of the ratio of wires to islands for all substrate vicinalities investigated. The plotted ratio of wires/islands is independent of the substrate vicinality. The slope of the line fit yields a mean activation energy of 1.4 eV.

reconstructions cause contrast in PEEM and can be imaged as bright zones during island decay (see the insets in figure 2). If anisotropic diffusion is present, as in the case of Ag on vicinal Si(001) [8], these zones are elongated in the direction of the lower diffusion barrier, i.e. along the step edges in the direction of the wires in the inset of figure 2(b).

For the wire formation, many parameters are relevant. Particularly important is the temperature, as the formation of Ag nanowires on flat and vicinal Si(001) substrates is temperature-dependent. When the temperature from one growth experiment to another is increased, the percentage of islands evolving into wires increases as well. Figure 3 shows the temperature dependence of the ratio of wires to islands. The Arrhenius-type graph unambiguously shows that the wire formation is thermally activated. The activation energy to form a wire is 1.4 eV higher than the activation energy needed to

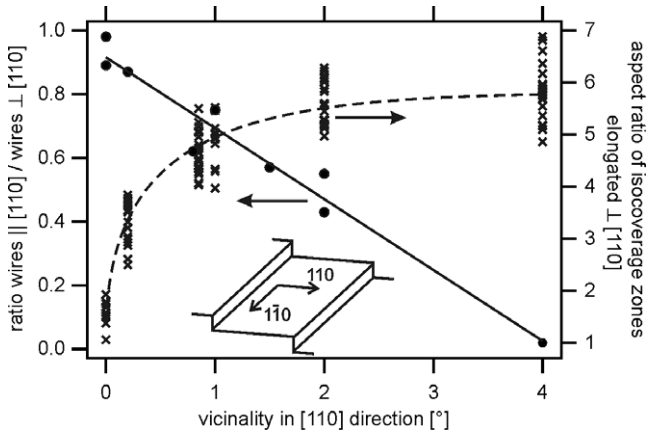

Figure 4. Vicinality dependence of the wire direction and the diffusion anisotropy. The solid line (left axis) shows the ratio of wires perpendicular and parallel to the steps. At higher vicinality, the wires align with the step edges. The dashed line (right axis) shows the aspect ratio of the diffusion field. The diffusion anisotropy increases with increased substrate vicinality [12]. The dashed line serves as a guide to the eye.

form a compact Ag island and is independent of the substrate's vicinality. In the investigated temperature range, the nucleation density changes dramatically for a constant flux. To eliminate any possible influences of the deposition rate on the probability of wire formation, we adjusted the deposition rate to yield a constant nucleation density for all experiments in figure 3. Furthermore, we investigated how the change in deposition rate would reflect on the ratio of wires/islands in figure 3. Surprisingly, at all temperatures and vicinalities investigated, the ratio of wires/islands was independent of the deposition rate, nucleation density, and vicinality.

Previous work [3] already reported that the wires overgrow the steps of the well-oriented Si(001) surface, and we can confirm that observation. On well-oriented Si(001) samples, wires are oriented randomly to the locally corrugated step edges, while they can overgrow many terraces. Nevertheless, the wires are always oriented along one of the two dimer directions. In contrast, on the 4° vicinal substrate, all wires form along the [1$\bar{1}$0] direction parallel to the step edges. The gradual transition from differently oriented wires to wires that are aligned with the step edges is illustrated in figure 4, where the ratio of wires growing in the two principal symmetry directions of the Si(001) surface is plotted as a function of the vicinality (solid line).

The dashed curve in figure 4 shows the aspect ratio of the isocoverage zones [11] for substrates of different vicinality [12]. The shape of the isocoverage zone is a measure of the diffusion anisotropy in the system. For samples of higher vicinality, we observe a higher diffusion anisotropy. While on a flat Si(001) surface the diffusion field is isotropic and the wires grow in both directions, on the 4° vicinal surface, the orientation of the anisotropy of the diffusion fields coincides with the exclusively observed nanowire direction.

4. Conclusions

Single-crystalline nanowires are formed on well-oriented and vicinal Si(001) substrates. The formation of these wires is temperature-dependent with an activation energy of 1.4 eV. During our growth experiments, we observed [4] shape transitions of an Ag island similar to those previously predicted from simulations [3]. Such transitions have been attributed to lattice mismatch between the Ag islands and the Si substrate. The measured activation energy for wire formation, however, is independent of the vicinality and stress is thus an unlikely candidate to cause the alignment of the wires with the steps. Instead, the attachment rates of diffusing Ag atoms might very well influence the direction in which the wires elongate. Earlier measurements [12] show that the diffusion anisotropy on a 4° vicinal surface has an activation energy of 0.7 eV, consistent with the effects of an Ehrlich–Schwoebel barrier [13, 14]. Since the step density increases with the vicinality, the mass transport over large distances across the surface steps becomes increasingly harder. On the flat substrates, with well-spaced steps running in arbitrary directions [15, 16], the wires grow in one of two possible directions with the same probability. But as the diffusion anisotropy and the step density grow and with increased angle of vicinality, the influence of the Ehrlich–Schwoebel barrier becomes more dominant. We therefore conclude that the nanowire's alignment is strongly influenced by anisotropic diffusion which, for the case of Ag/Si(001), is due to an Ehrlich–Schwoebel [13, 14] type barrier [12]. The anisotropic material deposition along one of the substrate's principal directions must be sufficient to cause the wires to preferentially grow along the fast diffusion direction, namely parallel to the step edges, as the diffusion anisotropy increases.

Nevertheless, the measured increase of the isocoverage zone's aspect ratio does not exhibit the linear dependence on the miscut that is found for the alignment of the nanowires (see figure 4). Since the step density is influenced by double-step [17] and Ag-induced multistep formation [18], it is almost impossible to quantify the diffusion anisotropy in terms of step density or terrace size. Furthermore, the aspect ratio of the isocoverage zone, as plotted in figure 4, is linked to the diffusion constants along and perpendicular to the steps in a nonlinear manner. There is a clear indication, however, even if the wire formation itself is caused by lattice mismatch strain, that the Ehrlich–Schwoebel barrier and the resulting diffusion anisotropy play a significant role in the predominant arrangement of the wires along the step edges for samples of higher vicinality.

Acknowledgments

Financial support from the Deutsche Forschungsgemeinschaft through no. SFB616 'Energy Dissipation at Surfaces' is gratefully acknowledged.

References

[1] Stahlmecke B, Meyer zu Heringdorf F J, Chelaru L I, Horn-von Hoegen M, Dumpich G and Roos K R 2006 *Appl. Phys. Lett.* **88** 053122
[2] Michely T, Reuter M C, Copel M and Tromp R M 1994 *Phys. Rev. Lett.* **73** 2095
[3] Tersoff J and Tromp R M 1993 *Phys. Rev. Lett.* **70** 2782

[4] Sindermann S, Wall D, Horn-von Hoegen M and Meyer zu Heringdorf F-J 2009 in preparation
[5] Li B Q, Swiech W and Zuo J M 2007 *Microsc. Microanal.* **13** 726
[6] Cho W S, Kim J Y, Park N G, Chae K H, Kim J W, Lyo I W, Kim S S, Choi D S and Whang C N 1999 *Surf. Sci.* **439** L792
[7] Kim Y W, Park N G, Cho W S, Chae K H, Whang C N, Kim K S, Kim S S and Choi D S 1998 *Surf. Sci.* **396** 295
[8] Roos K R, Roos K L, Horn-von Hoegen M and Meyer zu Heringdorf F-J 2005 *J. Phys.: Condens. Matter* **17** S1407
[9] Tromp R M and Reuter M C 1991 *Ultramicroscopy* **36** 99
[10] Bauer E 1994 *Rep. Prog. Phys.* **57** 895
[11] Roos K R, Roos K L, Lohmar I, Wall D, Krug J, Horn-von Hoegen M and Meyer zu Heringdorf F-J 2008 *Phys. Rev. Lett.* **100** 016103
[12] Wall D, Roos K R, Horn-von Hoegen M and Meyer zu Heringdorf F-J 2008 *Mater. Res. Soc. Symp. Proc.* **1088** 1088-W05-04
[13] Schwoebel R L and Shipsey E J 1966 *J. Appl. Phys.* **37** 3682
[14] Ehrlich G and Hudda F G 1966 *J. Chem. Phys.* **44** 1039
[15] Tersoff J and Pehlke E 1992 *Phys. Rev. Lett.* **68** 816
[16] Tromp R M and Reuter M C 1992 *Phys. Rev. Lett.* **68** 820
[17] Pehlke E and Tersoff J 1991 *Phys. Rev. Lett.* **67** 465
[18] Fölsch S, Winau D, Meyer G, Rieder K H, Horn-von Hoegen M, Schmidt T and Henzler M 1995 *Appl. Phys. Lett.* **67** 2185