Growth and structure characterization of EuSi$_2$ films and nanoislands on vicinal Si(001) surface

A. Seiler [a,b], O. Bauder [a,b], S. Ibrahimkutty [a,b], R. Pradip [a,b], T. Prüßmann [c], T. Vitova [c], M. Fiederle [a,d], T. Baumbach [a,b,e], S. Stankov [a,b,*]

[a] Institute for Photon Science and Synchrotron Radiation, Karlsruhe Institute of Technology, Eggenstein-Leopoldshafen, Germany
[b] Laboratory for Applications of Synchrotron Radiation, Karlsruhe Institute of Technology, Karlsruhe, Germany
[c] Institute for Nuclear Waste Disposal, Karlsruhe Institute of Technology, Eggenstein-Leopoldshafen, Germany
[d] Freiburg Materials Research Center, Freiburg, Germany
[e] ANKA, Angströmquelle Karlsruhe, Karlsruhe Institute of Technology, Eggenstein-Leopoldshafen, Germany

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ABSTRACT

Europium silicide nanoislands and films with Eu coverage in the range 0.3 ML 303 ML were grown on the vicinal Si(001) surface with 4° miscut towards [110] by molecular beam epitaxy. The nanostructures were characterized by atomic force microscopy, reflection high energy electron diffraction, *in situ* synchrotron radiation X ray absorption near edge structure spectroscopy and *ex situ* X ray diffraction. The analysis revealed the formation of EuSi$_2$ with a tetragonal structure. By increasing the Eu coverage the surface morphology gradually changes from isolated islands through films with very rough surface to thick films with smoother surface.

1. Introduction

Rare earth (RE) silicide nanostructures have been in the center of an intensive research since 1998 when Preinesberger et al. demon strated the self organization of DySi$_2$ in nanoclusters, nanoislands, and high aspect ratio nanowires upon deposition of sub monolayer amount of Dy on the clean Si(001) surface [1]. The metallic nature, very low Schottky barrier heights, enhanced chemical stability and single crystallinity along with the direct integration into the Si technology made the RE silicides very promising candidates for applications in optoelectronics, light emitting technology and nanoe lectronics as ohmic contacts and interconnects [2,3]. It has been demonstrated that depending on the growth conditions (substrate temperature during deposition, time and temperature of the post growth annealing) other RE metals also form silicides with various surface morphologies. A special attention has been paid on the stabilization of RE silicide nanowires with high aspect ratio. Up to now Dy [1 4], Ho [4], Er [5], Gd [6], and Sm [7] have been reported to self assemble in parallel nanowires on vicinal Si(001), while on the planar Si(001) surface the nanowires self organize along two orthogonal directions [8]. By changing the growth temperature 3D RE silicide nanoislands and clusters have been formed [1,9]. RE silicide films (Tb, Er) have first been studied by Baglin et al. [10] followed by investigations of Dy [11], Er [12 14] and Sm [15] silicide epitaxial films with thicknesses up to 1.2 μm.

Europium (Eu) is one of the most reactive rare earth metals and the only one among the lanthanides that exhibits a body centered cubic crystal lattice at ambient conditions [16]. The formation of Eu induced reconstruction at room temperature deposition of sub monolayer Eu coverage on vicinal and planar Si(100) surface has been investigated [17 19]. The interaction of Eu with the Si(111) surface and the early stage of silicide formation as a function of the substrate temperature have also been addressed, revealing a low diffusion rate of the Si atoms into the silicide film [20,21]. Here we present epitaxial growth and systematic investigation of the crystal structure and surface morphology of europium silicide films and nanoislands on vicinal Si(001) surface for Eu coverages ranging from 0.3 ML to 303 ML. By increasing the Eu coverage the surface morphology gradually changes from individual nanoislands through thin films with very rough surfaces to thick films with smoother surface. Traces of nanowires have not been found even for the lowest Eu coverage of 0.3 ML for the applied growth conditions. This is expected since the lattice mismatch in the studied system is very large implying that the nanowires formation is not very likely. In other RESi systems the nanowires formation is promoted by the

* Corresponding author at: Institute for Photon Science and Synchrotron Radiation, Karlsruhe Institute of Technology, Eggenstein-Leopoldshafen, Germany. Tel.: +49 72160828680; fax: +49 72160826172.
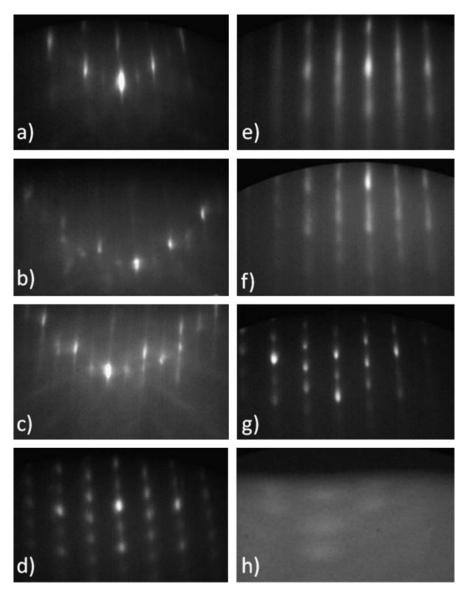*E-mail address:* Svetoslav.Stankov@kit.edu (S. Stankov).

Fig. 1. RHEED images recorded at the [110] azimuth of (a) clean Si(001) and for Eu coverages of (b) 0.3 ML, (c) 0.8 ML, (d) 3.0 ML, (e) 15.1 ML, (f) 60.6 ML, (g) 303 ML and (h) the RHEED image of the sample with Eu coverage of 30.3 ML deposited at room temperature and post-growth annealed at 600 °C for 10 min.

anisotropic lattice mismatch between the RE silicide with hexago nal symmetry and the Si substrate, meaning that the lattice mismatch is small ($< 1\%$) in one direction and large ($> 5\%$) in the perpendicular direction.

2. Experimental details

The samples were grown in an ultrahigh vacuum (UHV) chamber with a base pressure of 3×10^{-11} mbar located in the UHV Analysis lab at the synchrotron radiation facility ANKA. The n type (P doped, $10\,\Omega$ cm) Si(001) substrates with a miscut of $4°$ towards [110] supplied by MaTecK GmbH were resistively heated between 6 and 8 times to a temperature of 1200 °C for about 10 min in a separate UHV chamber with a base pressure of 5×10^{-10} mbar. During heating the pressure increased up to 5×10^{-9} mbar and recovered quickly to the starting values. The formation of a clean and well ordered (2×1) reconstructed Si(001) surface was verified by reflection high energy electron diffraction (RHEED) prior deposition of the reactive Eu. The clean Si(001) substrate was transferred under UHV conditions to the growth
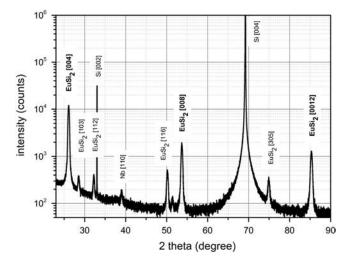

Fig. 2. X-ray diffraction scan on the sample with Eu coverage of 60.6 ML covered with 5.0 nm Nb layer. Single crystalline peaks (bold) are clearly visible. In addition, some polycrystalline peaks have been identified. Peaks arising from the Si(001) substrate and the Nb capping layer are also seen.

chamber where the deposition of Eu was carried out. A vacuum outgassed Eu metal, supplied by the Ames laboratory, was sub limated from an effusion cell using a pyrolytic boron nitride crucible that resulted in a pressure increase up to 3×10^{-10} mbar. The substrate temperature during deposition was kept at 400 °C. The samples were post growth annealed at 600 °C for 10 min to drive the reaction between the Eu and Si to completion. The growth rate was ~0.1 monolayer (ML) /min for the nanoislands and ~0.75 ML /min for the films. One ML is defined as 6.78×10^{14} atoms/cm^2 (the number of atoms per unit area on the Si(001) surface) which corresponds to an Eu coverage of 0.33 nm. Samples with the following Eu coverages were studied: 0.3 ML (0.1 nm), 0.8 ML (0.26 nm), 3.0 ML (1.0 nm), 15.1 ML (5.0 nm), 60.6 ML (20.0 nm), and 303 ML (100.0 nm). The nanostructures were characterized at room temperature with a RHEED instrument located in the growth chamber. The surface morphology was investigated with an Omicron SPM using contact mode atomic force microscopy (AFM) located in a separate
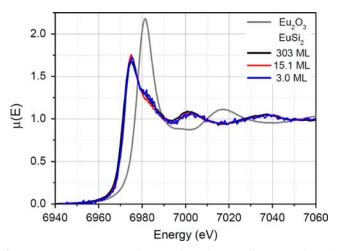

Fig. 3. Room temperature Eu L$_3$ edge X-ray absorption near edge structure (XANES) spectra of EuSi$_2$ with Eu coverage of 3.0, 15.1 and 303 ML. The spectrum of the Eu$_2$O$_3$ reference is shown for comparison.

UHV chamber with a base pressure 3×10^{-10} mbar connected to the growth chamber by a UHV transfer line. The sample with Eu coverage of 60.6 ML was covered with a 5.0 nm thick Nb layer to prevent oxidation and was investigated by *ex situ* X ray diffraction using X rays with wavelength 0.1541 nm (Cu K alpha1, Rigaku SmartLab).

In order to investigate the oxidation state of Eu, stoichiometry and structure of the europium silicide alloy the samples with coverage of 3.0 ML, 15.1 ML and 303 ML were studied by *in situ* (under UHV conditions) X ray absorption spectroscopy (XAS). X ray absorption near edge structure (XANES) measurements on the Eu L$_3$ absorption edge were performed at the INE Beamline of ANKA. A specially designed UHV chamber for X ray scattering and spectroscopy experiments with a base pressure 4×10^{-10} mbar was used for this experiment. Details on the instrument and the experimental setup can be found elsewhere [22].

3. Results and discussion

Fig. 1 summarizes the RHEED data recorded from the investi gated samples with the electron beam being parallel to the Si[110] azimuthal direction. The images are compared with that of a clean Si(001) surface (Fig. 1a). The sharp features and low background of the RHEED images (Fig. 1b g) reveal the formation of epitaxial single crystalline structures with good quality. It also points out to gradual changes that are taking place in the surface morphology, namely an evolution from islands (spots like pattern) towards films (more streaks like pattern) by increasing the Eu coverage. In addition to the main spots in the RHEED image of the sample with Eu coverage of 0.3 ML (Fig. 4b) superstructure spots are also visible. Kuzmin et al. [19], have demonstrated by systematic LEED studies that Eu induced (2×3) reconstruction appears at this coverage on the clean Si(100) surface, however, deposited at room temperature and post growth annealed at 600 °C for 10 min. It is very likely that the additional spots observed in Fig. 4b originate from (2×3) reconstructed surface as reported in [19] that coexists with the silicide alloy. The in plane lattice parameter obtained from the RHEED patterns is 4.28(9) Å that is in agreement with the
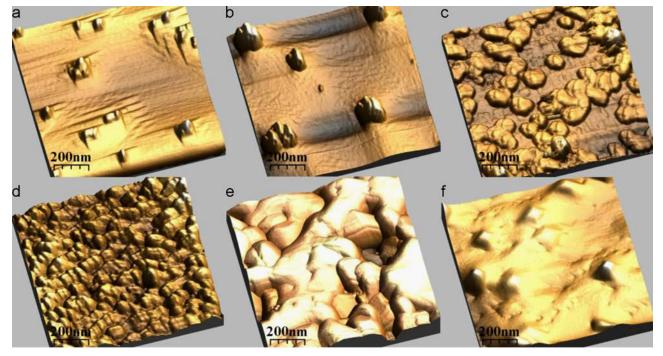

Fig. 4. 3D projections of the AFM images (1×1 µm^2) of EuSi$_2$ for Eu coverages of: (a) 0.3 ML, (b) 0.8 ML, (c) 3.0 ML, (d) 15.1 ML, (e) 60.6 ML, (f) 303 ML.

Table 1
Average sizes of the $EuSi_2$ islands for the indicated Eu coverages.

Eu coverage / ML	Average island sizes (length $\times$ width $\times$ height)/nm^3
0.3	$57 \pm 5 \times 64 \pm 5 \times 16 \pm 2$/isolated islands
0.8	$100 \pm 5 \times 105 \pm 5 \times 24 \pm 2$/isolated islands
3.0	$98 \pm 5 \times 92 \pm 5 \times 8 \pm 2$/clusters of islands

bulk value of 4.30 Å for $EuSi_2$ with tetragonal symmetry [23]. Therefore we conclude that, similarly to the other $RESi_2$ [24,25] the $EuSi_2$ grows with a 45° rotation relative to the Si unit cell, *i.e.* $EuSi_2[100] \| Si[110]$ on the $Si(001)$ surface. This rotation reduces the lattice mismatch from $+20.8\%$ to 12.0%.

An attempt for growth of europium silicide at room temperature has also been done. Fig. 1h shows the RHEED image of 30.3 ML Eu deposited at room temperature and annealed at 600 °C for 10 min. The observed diffuse halo and traces of Debye rings confirm the formation of a very rough polycrystalline film at these growth conditions.

To obtain a detailed structure information X ray diffraction study was performed on the sample with Eu coverage of 60.6 ML after deposition of 5.0 nm thick Nb layer to protect the alloy from oxidation. The data analysis (Fig. 2) confirm that the main phase is indeed the tetragonal $EuSi_2$ with the c axis being collinear to the [001] direction of the $Si(001)$, *i.e.* reflections [004], [008] and [0012]. However, contributions from other peaks are also visible indicating the presence of none negligible amount of polycrystal line $EuSi_2$. The lattice constant along the growth direction is found to be 13.68(7) Å that is in agreement with the expected bulk value of 13.66 Å for the tetragonal $I4_1/amd$ $EuSi_2$ structure [23].

Additional information about the stoichiometry and structure of the investigated nanostructures can be obtained from Eu L_3 edge XANES spectra measured *in situ* and at room temperature. The absorption features of the XANES spectra originate from multiple scattering of the photoelectron from the surrounding atoms, thereby fingerprinting the short and long range atomic order in the material. Fig. 3 shows the measured XANES spectra of the samples with Eu coverage of 3.0 ML, 15.1 ML and 303 ML and of the Eu_2O_3 reference sample. Extended X ray absorption fine structure (EXAFS) analysis reported in [22] confirms that the Eu sample with coverage of 303 ML exhibits $EuSi_2$ stoichiometry with a tetragonal crystal structure. Furthermore, the XANES spectra of the investigated samples, Fig. 3, are very similar implying that the Eu atom exhibits the same oxidation state of $2+$ in all samples and the Eu silicide alloy has the same stoichiometry and long and short range order corresponding to that of the tetragonal $EuSi_2$. The oxidation state of Eu in Eu_2O_3 is $3+$, therefore the spectrum of the reference sample clearly differs from that of the $EuSi_2$ samples.

In order to investigate the evolution of the surface morphology as a function of the Eu coverage a systematic study has been performed using an atomic force microscope working in a contact mode. Fig. 4 shows selected AFM images of the investigated samples. Fig. 4 a) and b) reveal the formation of isolated nanois lands for Eu coverages below 3.0 ML. The average length, width and height of the islands, including the errors, are summarized in Table 1. Increasing the Eu coverage from 3.0 to 15.1 ML results in the coalescence of the islands (Fig. 4c) in clusters that gradually transform into a film with very high roughness (Fig. 4d). At coverage of 303 ML the silicide forms a bulk like film with a smoother surface, (Fig. 4f). However, one has to note that by using a contact mode AFM it is likely that an interaction between the tip

and the surface takes place that could influence to a certain extend the shape of the investigated nanoobjects. Such artefacts can be seen in Figs. 4c and f.

4. Conclusions

We have grown europium disilicide islands and films on vicinal Si (001) surface with a miscut of 4° towards [110] by Eu deposition at 400 °C followed by a post growth annealing at 600 °C for 10 min. A systematic AFM study reveals that for Eu coverages below 3.0 ML well isolated nanoislands are formed. At coverages between 3.0 ML and 60.6 ML of Eu islands coalescence takes place leading to the formation of films with very rough surface. A further increase of the Eu coverage reduces notably the film roughness. The *in situ* reflection high energy electron diffraction and X ray absorption near edge structure spectroscopy studies unambiguously confirm the formation of single crystalline $EuSi_2$ with tetragonal structure. This is verified by *ex situ* X ray diffraction that also reveals the presence of a minor polycrystalline fraction of europium disilicide.

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