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Platinum passivation of self-assembled erbium disilicide nanowire arrays on Si(001)

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ABSTRACT Self-assembled $ErSi_{2-x}$ nanowires were grown on Si(001) substrates with an average nanowire width of 2.8 nm. Submonolayer coverage of platinum was deposited on the Si(001) surface post $ErSi_{2-x}$ growth. Scanning tunneling microscopy and reactive ion etching showed that platinum preferentially deposited on the nanowire surface versus the Si surface. Reactive ion etching of $ErSi_{2-x}$ nanowires with and without platinum on the surface demonstrated that platinum acted as a more resistant etch mask than $ErSi_{2-x}$. $Pt/ErSi_{2-x}$ nanowires are air stable whereas $ErSi_{2-x}$ nanowires decompose after exposure to ambient for five weeks.

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1 Introduction

Research in semiconductor physics is undergoing a paradigm shift. A bottom-up or self-assembly approach is being investigated as an alternative to the current top-down lithographic approach. Most significantly, the shift from the exclusive use of lithography for device fabrication opens the field to not only novel fabrication schemes but also to the incorporation of diverse material systems. Hexagonal rare earth disilicide ($RESi_{2-x}$) nanowires self-assemble during epitaxial growth as one-dimensional nanostructures on Si(001) substrates due to an anisotropic lattice mismatch with Si[110] [1]. Total energy minimization drives the system to form these one-dimensional nanostructures along Si[110]. The length of coherently strained nanowires is dependent on surface kinetics while the wire width is thermodynamically limited via strain energy [2]. On flat Si(001) substrates, $RESi_{2-x}$ (RE = Dy [2–4], Er [2, 5], Gd [2, 6]) nanowires grow in two orthogonal directions due to the double domain 2×1 reconstructed Si(001) surface. We have demonstrated that dense arrays of parallel $RESi_{2-x}$ (RE = Er, Dy, Sm) nanowires exhibiting high aspect ratios, having lengths exceeding 1 micron and widths less than 5 nm can be grown on vicinal Si(001) substrates with a miscut of 2.5° toward the [110] azimuth [7]. Vicinal Si(001) substrates with a tilt greater than 2° toward the [110] azimuth exhibit double atomic steps with a single domain 2×1 reconstructed surface, that is, Si dimer rows run orthogonal to the step edge [8]. $RESi_{2-x}$ nanowires grow perpendicular to the Si dimer rows and therefore form parallel arrays on vicinal Si(001) substrates. In bulk form and in thin films, $RESi_{2-x}$ are good conductors, $\varrho \sim 0.1\ \mu\Omega\,\mathrm{cm}$, with a low Schottky barrier to *n*-type silicon. Unfortunately, $RESi_{2-x}$ oxidize rapidly in air. The highly reactive surface limits applications for $RESi_{2-x}$ nanowires. If these nanowires are going to be used as interconnects in nanoscale devices, they must be air stable.

In this paper, we demonstrate that platinum passivates the $ErSi_{2-x}$ nanowire surface. Scanning tunneling microscopy (STM) shows that Pt forms clusters on the $ErSi_{2-x}$ nanowire surface. Scanning electron microscopy (SEM) images taken after reactive ion etching (RIE) of these nanostructures show that Pt preferentially wets the nanowire surface versus Si and acts as an etch mask. $ErSi_{2-x}$ nanowires without Pt on the surface are significantly etched whereas the Pt coated nanowires are not. The achievement of a high density, $10^{11}\ \mathrm{cm}^{-2}$, of self-assembled metal nanostructures coupled with self-assembled molecular monolayers (ML) is an important precursor to forming molecular sensing, memory and logic devices with density and features sizes not attainable using conventional lithography.

2 Experiment

$ErSi_{2-x}$ nanowires were grown on flat Si(001) substrates in ultrahigh vacuum. The chamber base pressure was 1×10^{-10} Torr. The 2×1 reconstructed Si(001) surface was prepared by resistively heating the sample to 1150 °C for 20 s at a chamber pressure of less than 1×10^{-9} Torr, rapidly reducing the temperature to 600 °C, and then slowly cooling to room temperature. Er metal was deposited from an electron beam evaporator on a Si(001) substrate heated to a temperature of 600 °C. The Er coverage was approximately 0.15 ML as determined from ex situ Rutherford backscattering (RBS) analysis to calibrate the ion flux with the surface coverage. The pressure during deposition was kept below 1×10^{-9} Torr. $ErSi_{2-x}$ was formed as a reaction takes place between the Si on the surface and the deposited Er metal. STM images were taken in situ both before and after Er deposition. The sample voltage with respect to the tip during STM imaging was

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2.0 V and the images were obtained under a constant tunneling current of 0.1 nA at room temperature. Pt was deposited at room temperature on the surface after $ErSi_{2-x}$ nanowire formation. The sample was then annealed at 550 °C for 10 min. STM images were also obtained after Pt deposition. Samples with $ErSi_{2-x}$ nanowires and $Pt/ErSi_{2-x}$ nanowires were removed from the UHV system and were exposed to ambient briefly and stored in a dry nitrogen environment for a period of approximately one day or less and then etched using RIE in CHF_3 gas for 45 s. SEM and atomic force microscopy (AFM) images were obtained before and after etching to view the evolution of the surface structure. AFM was also used to monitor the reactivity of the surface after exposure to air for periods between five to eight weeks.

3 Results and discussion

An AFM image is shown in Fig. 1a of an $ErSi_{2-x}$ nanowire immediately after removing the sample from vacuum. In comparison, Fig. 1b shows the change in the surface morphology after the sample has been exposed to air for five weeks. The nanowire surface has roughened considerably which was attributed to oxidation of $ErSi_{2-x}$. In Fig. 2a, a high resolution STM image of the $ErSi_{2-x}$ nanowire surface taken in situ is shown. The $c(2 \times 2)$ surface reconstruction that is characteristic of the hexagonal lattice is observable. In comparison, a STM image of the nanowire surface after room temperature Pt deposition and post growth annealing at

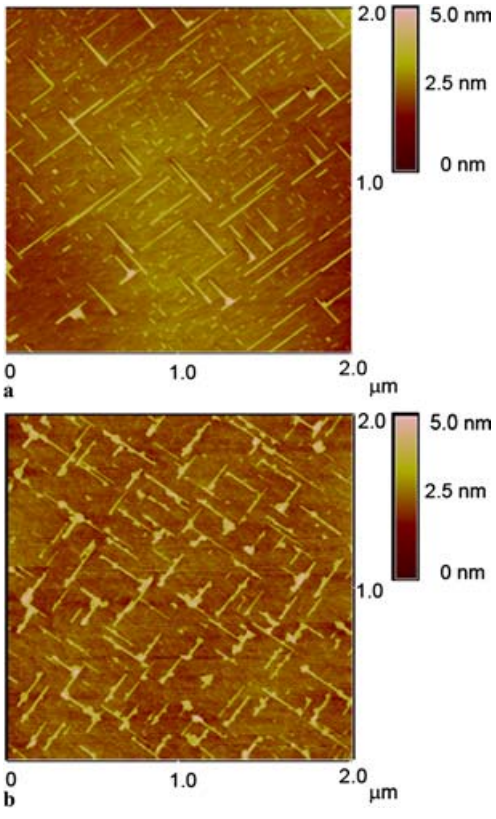

FIGURE 1 $2\,\mu m \times 2\,\mu m$ AFM images of $ErSi_{2-x}$ nanowire arrays on Si(001) taken (**a**) immediately after removal from the vacuum system and (**b**) after sitting in ambient for five weeks

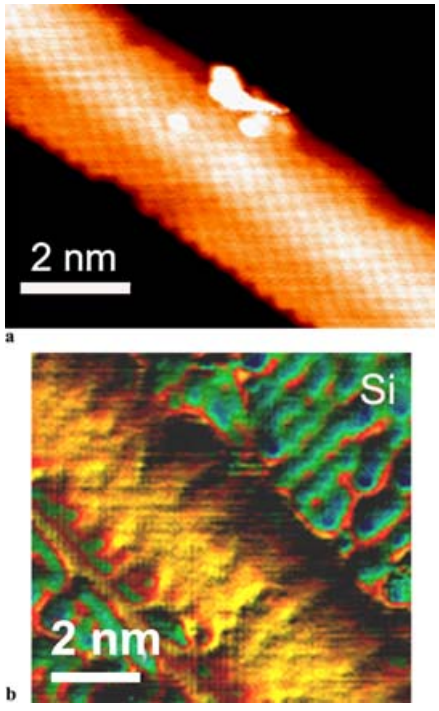

FIGURE 2 10 nm × 10 nm STM images of $ErSi_{2-x}$ nanowires on Si(001): (**a**) Before Pt deposition the $c(2 \times 2)$ surface reconstruction is visible on the nanowire. (**b**) After Pt deposition and annealing at 550 °C the $c(2 \times 2)$ surface reconstruction is gone but the Si (2×1) surface reconstruction is still evident in the upper left corner

550 °C is shown in Fig. 2b. The STM image of the Pt coated $ErSi_{2-x}/Si(001)$ surface has two significant features. First the $c(2 \times 2)$ surface reconstruction is no longer discernible on the nanowire surface. Second, the 2×1 surface reconstruction is still evident on the Si surface next to the nanowire. In contrast, sub monolayer coverage of Pt on a bare Si(001) substrate induce disorder of the 2×1 surface reconstruction for coverage less than 1/6 ML and induce a $c(4 \times 2)$ and $c(4 \times 6)$ surface reconstruction for coverage greater than 1/6 ML [9]. The Pt coverage on the surface is 0.1 ML as ascertained from ex situ RBS data to calibrate the Er coverage with measured ion current. The coverage of Pt on the nanowire surface appears continuous in this STM image. Therefore, based on the total amount of Pt detected on the surface, it appears that Pt preferentially deposits on the nanowire surface versus the Si(001) substrate.

Further evidence of preferential Pt deposition on the $ErSi_{2-x}$ nanowire surface is obtained from SEM and AFM images taken before and after RIE of the surface. Samples with only $ErSi_{2-x}$ nanowires on the Si(001) surface and samples with Pt deposited on $ErSi_{2-x}$ nanowires on the Si(001) surface were etched in CHF_3 gas for 45 s. A STM image of $ErSi_{2-x}$ nanowire arrays before etching is seen in Fig. 3a. The average $ErSi_{2-x}$ nanowire length is approximately 200 nm. After RIE, the SEM image of Fig. 3b illustrates that the nanowires are partially etched in CHF_3 gas. The nanowire length has decreased significantly. In comparison, Fig. 3c shows the STM image of the $Pt/ErSi_{2-x}$ nanowires arrays on Si(001). Again the average nanowire length is approximately 200 nm. Figure 3d shows an SEM image of $Pt/ErSi_{2-x}$ nanowires after a similar RIE treatment. The majority of $Pt/ErSi_{2-x}$

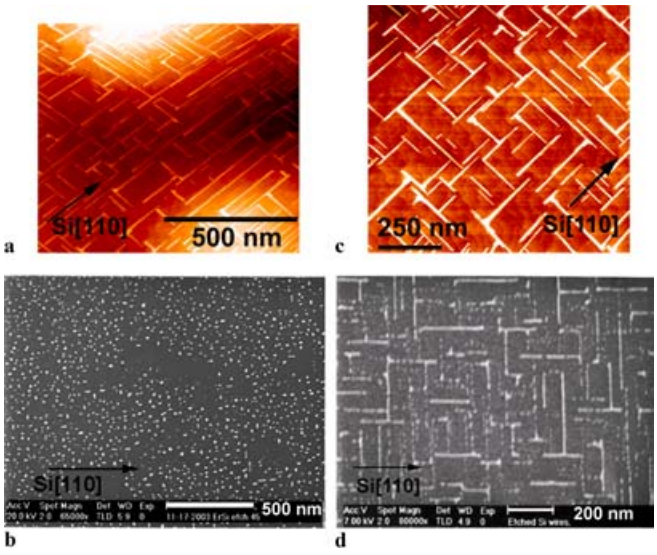

FIGURE 3 $ErSi_{2-x}$ nanowire arrays on Si(001): (**a**) STM image and (**b**) SEM image after etching in CHF_3 gas for 45 s. $Pt/ErSi_{2-x}$ nanowire arrays on Si(001): (**c**) STM image and (**d**) SEM image after etching in CHF_3 gas for 45 s

nanowires remain intact after etching. AFM images were obtained both before and after etching the nanowires to measure the change in nanowire feature height. The average feature height changed from 1.0 nm to 7.8 nm for Pt coated $ErSi_{2-x}$ nanowires and from 1.0 nm to 5.8 nm for the remaining $ErSi_{2-x}$ nanowires with etching.

In Fig. 3d, some $Pt/ErSi_{2-x}$ nanowires are seen to be segmented after the RIE step. The nanowires that break up into segments or linear chains of quantum dots may arise from incomplete Pt coverage on the surface. STM images prior to etching show clusters on some of the nanowire surfaces. These nanowires may have incomplete Pt coverage. In Fig. 4, a 15 nm × 15 nm STM image is shown in which the clusters on the nanowire surface are resolvable. The clusters form an angle of approximately $34.6 \pm 4.6(1\sigma)$ degrees with respect to the long axis of the nanowire. The cluster arrangement on the nanowire surface as observed in STM images is consistent with planar clusters of Pt atoms on the surface. This can be understood by comparing the nearest neighbor distance of Pt atoms with that of $ErSi_{2-x}$. The lattice constant of Pt in the face centered cubic (fcc) lattice is 0.3924 nm and that of $ErSi_{2-x}$ in the hexagonal lattice is 0.4088 nm along [0001] and 0.3798 nm along $[11\bar{2}0]$. Due to the anisotropic lattice mismatch with $Si[1\bar{1}0]$, the long axis of the nanowire is oriented along $[11\bar{2}0]$ or the *a* axis of the hexagonal lattice [1]. The planes that run at an angle of 38.8° with the *a* axis of the hexagonal lattice are the $[\bar{1}2\bar{1}3]$ planes and the interplanar spacing of these planes is 0.256 nm. The nearest neighbor spacing of fcc Pt is 0.277 nm but the calculated nearest neighbor spacing for clusters of Pt atoms from density functional theory calculations is 0.258 nm, 0.273 nm, and 0.261–0.265 nm for clusters of four, five and six atoms, respectively, and the lowest energy state is in a planar configuration [10]. Thus when the Pt coverage is incomplete on the nanowire surface, it may be energetically favorable for Pt atoms to assemble into a particular cluster size such that the nearest neighbor spacing most closely matches with the $ErSi_{2-x}$ hexagonal lattice. This type of size selection can be exploited in the future to form arrays of metallic quantum dots on Si(001) with a very narrow size distribution. $ErSi_{2-x}$ nanowires that are continuously coated with Pt appear highly strained; AFM images of $Pt/ErSi_{2-x}$ nanowires that were not etched in the RIE process described above show evidence that the nanowires have delaminated from the surface after sitting in UVH for seven days. The AFM images have pits on the surface with the approximate width of $Pt/ErSi_{2-x}$ nanowires seen in STM. These pits were not observable in AFM images of surfaces with bare $ErSi_{2-x}$ nanowires or with $Pt/ErSi_{2-x}$

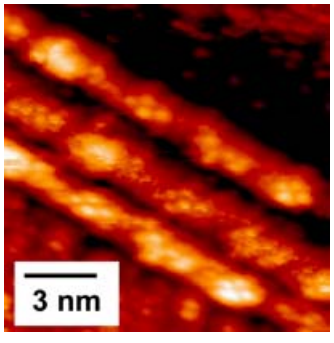

FIGURE 4 15 nm × 15 nm STM image of clusters on the $ErSi_{2-x}$ nanowire surface after Pt room temperature deposition and anneal at 550 °C. The clusters form an angle of 34.6° with the long axis of the nanowire

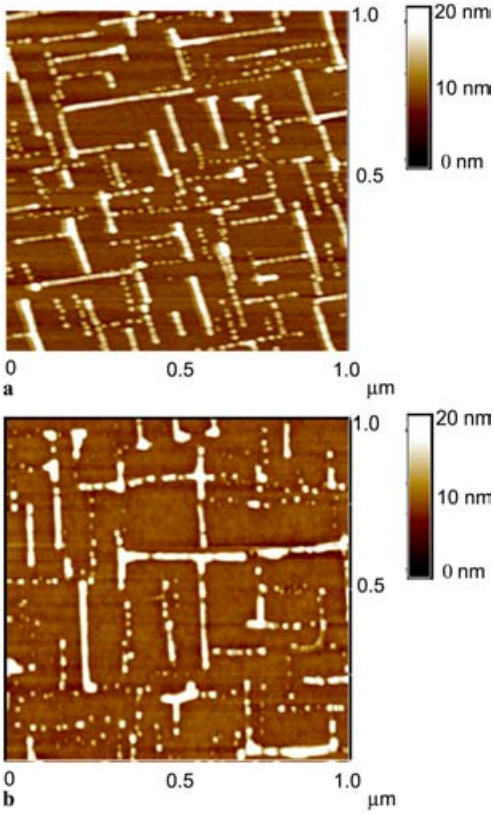

FIGURE 5 1 μm × 1 μm AFM images of $Pt/ErSi_{2-x}$ nanowire arrays on Si(001) taken (**a**) immediately after RIE and (**b**) after sitting in ambient for 8 weeks

nanowires that were treated with RIE within two days after preparation. The RIE etch into the Si substrate allows for relaxation of the Si lattice underneath the nanowire and reduce the strain in the $ErSi_{2-x}$ nanowire.

In order to determine stability of the Pt coated nanowires, AFM images were obtained immediately after etching, Fig. 5a, and after sitting in ambient for eight weeks, Fig. 5b. The surface morphology does not change for the Pt coated $ErSi_{2-x}$ nanowires as it did for the bare $ErSi_{2-x}$ nanowires seen in Fig. 1. Thus, Pt acts as a passivating layer.

4 Conclusion

STM images of Pt deposited on $ErSi_{2-x}$ nanowires fabricated on Si(001) substrates indicate that Pt preferentially deposits on the nanowire surface versus the Si(001) surface. SEM and AFM images confirm that Pt acts as an etch mask for the nanowire surface but not the Si(001) substrate. Future work will be performed to tune the Pt coverage to select metallic quantum dot arrays or nanowire arrays. We have also demonstrated that the deposition of Pt on an $ErSi_{2-x}$/Si(001) surface produces air stable metallic nanowires. These self-assembled nanostructures can be used a templates to fabricate hybrid organic-inorganic nanodevices with sensing or computing applications.

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