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Platinum/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 average nanowire width of 2.8 nm. Submonolayer coverage of platinum was deposited postgrowth. Scanning tunneling microscopy 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. Etching platinum coated nanowires with lower platinum coverage produced linear arrays of quantum dots with a diameter of approximately the pre-etched nanowire width. The platinum layer was shown to passivate the highly reactive rare earth disilicide surface.**

Index Terms — **Epitaxial growth, nanotechnology, rare earth alloys, Schottky barriers, semiconductor-metal interfaces, quantum dots, quantum wires.**

I. 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 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, $\rho \sim 0.1\ \mu\Omega$ 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 shows that Pt acts as an etch mask. $ErSi_{2-x}$ nanowires without Pt on the surface are significantly etched whereas the Pt coated nanowires are not. In addition, etching $ErSi_{2-x}$ nanowires with a lower Pt coverage produced quantum dot arrays with a narrow size distribution where the quantum dot diameter is related to the nanowire width. The achievement of a high density, 10^{11} 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.

II. 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 seconds at a chamber pressure of less than 1×10^{-10} 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 are taken *in situ* both before and after Er deposition. The sample voltage with respect to the tip during STM

imaging was 2.0 V and the images were obtained under a constant tunneling current of 0.1 nA at room temperature. Pt was deposited on the surface after nanowire formation at room temperature. 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 vacuum and were etched using RIE in CHF_3 gas for 45 seconds. SEM and atomic force microscopy (AFM) images were obtained before and after etching to view the evolution of the microstructure.

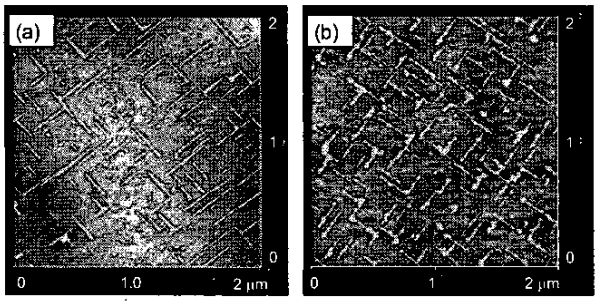

Fig. 1. 2 μm × 2 μm AFM images of $ErSi_{2-x}$ nanowire arrays on Si(001) taken (a) immediately after removal from the vacuum system and (b) after sitting in ambient for 5 weeks.

III. Results and Discussion

An AFM image is shown in Fig. 1(a) of an $ErSi_{2-x}$ nanowire immediately after removing the sample from vacuum. In comparison, Fig. 1(b) shows the change in the surface morphology after the sample has been exposed to air for 5 weeks. The nanowire surface has roughened considerably which was attributed to oxidation of $ErSi_{2-x}$. In Fig. 2(a), a high resolution STM image of the $ErSi_{2-x}$ nanowire surface taken *in situ* is shown. The c (2 × 2) surface reconstruction that is characteristic of the hexagonal lattice is observable. In comparison, an STM image of the nanowire surface after room temperature Pt deposition and postgrowth annealing at 550° C is shown in Fig. 2(b). The STM image of the Pt coated $ErSi_{2-x}/Si(001)$ surface has two significant features. First the c (2 × 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, submonolayer coverages of Pt on a bare Si(001) substrate induces disorder of the 2 × 1 surface reconstruction for coverages less than 1/6 ML and induce a c(4 × 2) and c(4 × 6) surface reconstruction for coverages 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 STM images. 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(00) substrate.

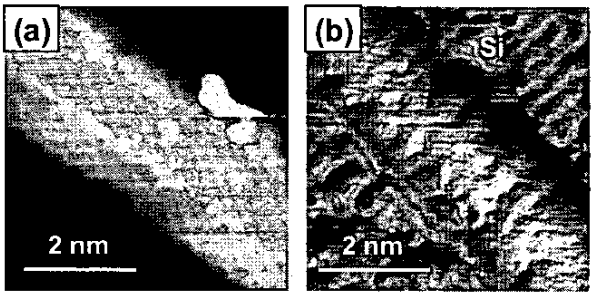

Fig. 2. 10 nm × 10 nm STM images of $ErSi_{2-x}$ nanowires on Si(001): (a) Before Pt deposition the c(2 × 2) surface reconstruction is visible on the nanowire. (b) After Pt deposition and annealing at 550° C the c(2 × 2) surface reconstruction is gone but the Si (2 × 1) surface reconstruction is still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

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 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 seconds. A STM image of $ErSi_{2-x}$ nanowire arrays before etching is seen in Fig. 3(a). The average $ErSi_{2-x}$ nanowire length is approximately 200 nm. After RIE, the SEM image of Fig. 3(b) illustrates that the nanowires are partially etched in CHF_3 gas. The nanowire length has decreased significantly. In comparison, Fig. 3(d) shows an SEM image of Pt/ $ErSi_{2-x}$ nanowires after a similar RIE treatment. The majority of Pt/ $ErSi_{2-x}$ 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. In order to determine stability of the Pt coated nanowires AFM images were obtained after etching and after sitting in ambient for 8 weeks. The surface morphology does not change for the Pt coated $ErSi_{2-x}$ nanowires. Thus, Pt acts as a passivating layer.

Nanowires with a lower coverage of Pt on the surface formed arrays of quantum dots aligned along Si[110] with a very narrow size distribution after RIE as seen in Fig 4.

STM images prior to etching show that Pt forms clusters on the nanowire surface. When the coverage of Pt is incomplete on the nanowire surface, the cluster size appears to be related to the nanowire width. Since Pt acts as an etch mask the quantum dots have a narrow size distribution around the diameter of the pre-etched nanowire.

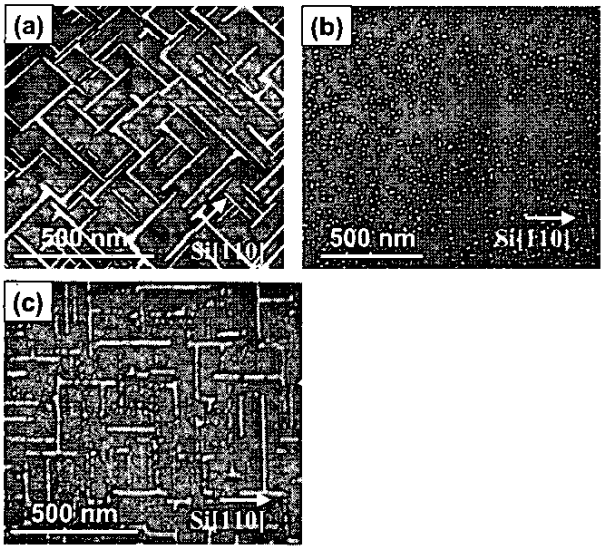

Fig. 3. (a) STM image of $ErSi_{2-x}$ nanowire arrays on Si(001). SEM images of (b) $ErSi_{2-x}$ nanowire arrays and (c) Pt/ $ErSi_{2-x}$ nanowire arrays after etching in CHF_3 gas for 45 seconds.

VII. 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. SEM and AFM images confirm that Pt acts as an etch mask for the nanowire surface but not the Si(001) substrate. We have demonstrated that the deposition of Pt on an $ErSi_{2-x}$/Si(001) surface produces air stable metallic nanowires. In addition, RIE of $ErSi_{2-x}$ nanowires with lower coverages of Pt on the surface produces ordered arrays of metallic quantum dots aligned along Si[110]. These self-assembled nanostructures can be used a templates to fabricate hybrid organic-inorganic nanodevices with sensing or computing applications.

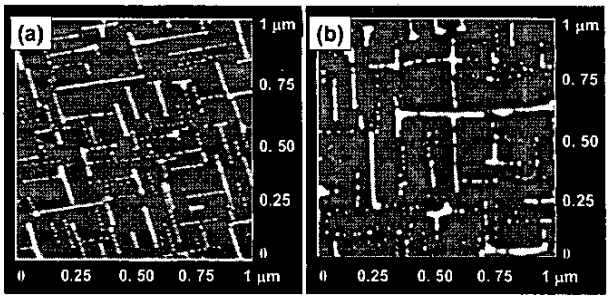

Fig. 4. 1 μm × 1 μm AFM images of Pt/$ErSi_{2-x}$ nanowire arrays on Si(001) taken (a) immediately after RIE and (b) after sitting in ambient for 8 weeks.

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References

[1] Y. Chen, D. A. A. Ohlberg, G. Medeiros-Ribeiro, Y. A. Chang, and R. S. Williams, Appl. Phys. Lett. **76**, 4004 (2000).

[2] Y. Chen, D. A. A. Ohlberg, and R. S. Williams, J. Appl. Phys. **91**, 3213 (2002).

[3] C. Preinesberger, S. K. Becker, S. Vandré, T. Kalka, and M. Dähne, J. Appl. Phys. **91**, 1695 (2002).

[4] J. Nogami, B. Z. Liu, M. V. Katkov, C. Ohbuchi, and N. O. Birge, Phys. Rev. B **63**, 233305 (2001).

[5] Y. Chen, D. A. A. Ohlberg, G. Medeiros-Ribeiro, Y. A. Chang, and R. S. Williams, Appl. Phys. A **75**, 353 (2002).

[6] D. Lee and S. Kim, Appl. Phys. Lett. **82**, 2619 (2003).

[7] R. Ragan, Y. Chen, D. A. A. Ohlberg, G. Medeiros-Ribeiro, and R. S. Williams, J. Cryst. Growth **251**, 657 (2003).

[8] D. J. Chadi, Phys. Rev. Lett. **59**, 1691 (1987).

[9] H. Itoh, S. Narui, A. Sayama, and T. Ichinokawa, Phys. Rev. B **45**, 11136 (1992).