Bias-dependent scanning tunneling microscopy study of the oxygen-adsorbed Si(111)-(7×7) surface: Observation of metastable molecular oxygen

Kazuyuki Sakamoto, S. Torbjörn Jemander, Göran Hansson and Roger Uhrberg

Linköping University Post Print

N.B.: When citing this work, cite the original article.

Original Publication:

Kazuyuki Sakamoto, S. Torbjörn Jemander, Göran Hansson and Roger Uhrberg, Bias-dependent scanning tunneling microscopy study of the oxygen-adsorbed Si(111)-(7×7) surface: Observation of metastable molecular oxygen, 2002, Physical Review B. Condensed Matter and Materials Physics, (65), 15, 155305.

<http://dx.doi.org/10.1103/PhysRevB.65.155305>

Copyright: American Physical Society

<http://www.aps.org/>

Postprint available at: Linköping University Electronic Press

<http://urn.kb.se/resolve?urn=urn:nbn:se:liu:diva-47885>

Bias-dependent scanning tunneling microscopy study of the oxygen-adsorbed Si(111)-(7×7) surface: Observation of metastable molecular oxygen

Kazuyuki Sakamoto,^{1,2,*} S. Thorbjörn Jemander,¹ Göran V. Hansson,¹ and Roger I. G. Uhrberg¹

¹*Department of Physics and Measurement Technology, Linköping University, S-581 83 Linköping, Sweden*

²*Department of Physics, Graduate School of Science, Tohoku University, Sendai, 980-8578, Japan*

(Received 17 May 2001; revised manuscript received 14 November 2001; published 26 March 2002)

We have observed the initial stage of oxygen adsorption on a Si(111)-(7×7) surface using scanning tunneling microscopy. Among the bright sites observed after exposing the surface to oxygen in occupied state images, there are differences in the bias dependence of the brightness. Taking into account the local density of states of the oxygen-adsorbed Si(111)-(7×7) surface, we conclude that the sites appearing brightly only with a tip bias of $\geq +2.1$ V are the molecular oxygen. The preferred adsorption site of this molecular species is a corner adatom, which has an oxygen atom adsorbed into its backbond, of the faulted half of the (7×7) unit cell.

DOI: 10.1103/PhysRevB.65.155305

PACS number(s): 68.37.Ef, 68.43.-h, 73.20.At, 73.20.Hb

I. INTRODUCTION

As motivated by the technological importance of thin silicon oxide films in semiconductor devices, the initial stage of oxygen adsorption on silicon surfaces has been a topic of experimental and theoretical investigations. One of the most important issues of the initial chemisorption stage is the presence of metastable oxygen adsorbed on the Si(111)-(7×7) surface, whose lifetime is reported to be from approximately 10 min^{1–4} to several hours.^{5–10}

This metastable species was observed using various spectroscopic experiments, e.g., near-edge x-ray absorption fine structure (NEXAFS),^{2,3} ultraviolet photoelectron spectroscopy (UPS),^{3–7,12,13} x-ray photoelectron spectroscopy,^{3,9} and high-resolution electron-energy-loss spectroscopy (HREELS).^{10,11} In the early studies, the metastable species is reported to be a molecular species, the so-called “molecular precursor,” which is adsorbed on top of an atom of a clean Si(111)-(7×7) surface. However, the quite recent NEXAFS (Ref. 2) and UPS (Ref. 12) studies state that the metastable species is adsorbed on top of an adatom stabilized by an oxygen atom coadsorbed into the backbond. That is, the metastable oxygen is not a precursor and interacts only with the dangling bonds modified by the adsorption of an oxygen atom into the backbond.

Compared to the spectroscopic experiments, scanning tunneling microscopy (STM) studies have been mainly focused on the surface modified by atomic oxygen.^{13–18} Until now, three STM studies have reported the observation of the molecular oxygen.^{19–21} In one study,¹⁹ Dujardin *et al.* assigned the bright sites observed in the unoccupied state image with a sample biased at +2 V to the molecular species. However, this assignment does not agree with the scanning tunneling spectroscopy (STS) study,¹³ in which the bright sites observed using the same sample bias voltage are stated to be the adatom with an oxygen atom adsorbed into a backbond. The second STM study reports the observation of the molecular oxygen at a temperature of 620 K,²⁰ though the metastable states originating from the molecular species were reported to disappear at a temperature lower than 600 K

using NEXAFS,² XPS,³ HREELS,¹¹ and UPS.¹² Further, in the second study, the bright sites observed in the occupied state images at a sample bias of -1 V are assigned to the molecular species, though the molecular oxygen has no density of states at the corresponding binding energy.¹² In the third study,²¹ Martel *et al.* reported the presence of two adsorption sites for the molecular species, i.e., the on top site of an adatom that has an oxygen atom adsorbed into its backbond and the on top site of a rest atom. However, only one adsorption site, the on top site of an adatom that has an oxygen atom adsorbed into its backbond, is reported in the recent spectroscopic studies.^{2,12} Thus, despite the large number of STM studies, there is no observation of the metastable molecular species, which is consistent with spectroscopic studies.

One method to observe the molecular oxygen with certainty is to compare the electronic structures of the oxygen induced bright and/or dark sites with the spectroscopic results. In this paper, we present a bias-dependent STM study of the oxygen-adsorbed Si(111)-(7×7) surface. Among the bright sites observed in the occupied state image after exposing the clean Si(111)-(7×7) surface to oxygen, there are differences in the bias dependence of the brightness that indicate different local densities of states at these sites. Taking the previous UPS results into account,^{3,12} we conclude that the bright sites observed only with a tip bias of $\geq +2.1$ V in the occupied state images are the molecular oxygen species. This molecular species adsorbs preferentially at a corner adatom site, which has an oxygen atom adsorbed into its backbond, of the faulted half.

II. EXPERIMENTAL DETAILS

The measurements were performed in an ultrahigh-vacuum (UHV) chamber, using a homemade room-temperature STM.²² A connected preparation UHV chamber that is equipped with a low-energy electron diffraction (LEED) system, an Auger-electron spectrometer (AES), and a quadrupole mass spectrometer (QMS) was used to prepare the clean Si surface. The base pressures were below 5×10^{-11} Torr in both chambers. The Si(111) sample, cut

FIG. 1. 15.6 nm $\times$ 15.6 nm occupied state STM image of a clean Si(111)-(7 $\times$ 7) surface. The tip bias is +2.1 V, and the tunneling current is 0.15 nA. The (7 $\times$ 7) unit cell is indicated in the upper right corner of the figure. The faulted half is indicated by F and the unfaulted one by UF.

from an Sb-doped (*n*-type) Si wafer, was preoxidized chemically before it was inserted into the vacuum system. To obtain the clean reconstructed Si(111)-(7 $\times$ 7) surface, the sample was resistively heated to 1420 K in the UHV chamber. The quality of the surface structure was checked by the observation of a clear (7 $\times$ 7) LEED pattern and the cleanliness was verified by AES before transferring the sample into the STM chamber under UHV conditions. After that, we first confirmed the quality and the cleanliness of the Si(111)-(7 $\times$ 7) surface using STM before the O₂ exposure. No additional H₂O, CO, or CO₂ was detected by the QMS during the O₂ exposure. All STM images were obtained in the constant-current mode at room temperature.

III. RESULTS AND DISCUSSION

In this STM study, we observed the occupied state images of the sample with a positive tip bias for the following three reasons. First, to discuss the electronic states of the sites observed in the STM images, we have to compare our bias-dependent results with the occupied states observed in UPS.^{3–7,12,13} Second, since the use of a negatively biased tip results in the injection of electrons into the antibonding π_g and/or $3\sigma^*$ orbitals of the metastable molecular oxygen, there is a possibility to dissociate the molecules, which would make it harder to observe the metastable molecules. Finally, it is easier to obtain information on the reactivity of the faulted and unfaulted halves of the dimer-adatom stacking-fault (DAS) structure²³ by measuring the occupied electronic states rather than the unoccupied ones.²⁴ Figure 1 shows the occupied state STM image of a clean Si(111)-(7 $\times$ 7) surface obtained with a tip bias of +2.1 V. The (7 $\times$ 7) unit cell is indicated in the upper right corner of the figure, and the 12 adatoms are clearly observed in the unit cell. In addition, we are able to recognize the faulted and unfaulted halves of the DAS structure²³ by the different

FIG. 2. 31.2 nm $\times$ 31.2 nm occupied state STM image of a 0.1-L O₂-exposed Si(111)-(7 $\times$ 7) surface. The tip bias is +2.1 V, and the tunneling current is 0.15 nA.

brightness of the two halves. The faulted half is indicated by F and the unfaulted one by UF in the unit cell indicated in the figure. Moreover, we observe a dark site indicated by an arrow in Fig. 1. This dark site is either a missing adatom site formed during the cleaning process of the sample or created by the adsorption of some foreign species on top of the adatom. The observation that less than 0.4% of the adatom sites are dark verifies the high quality and cleanliness of the Si(111)-(7 $\times$ 7) surface.

An occupied state image of the O₂-exposed Si(111)-(7 $\times$ 7) surface obtained with a tip bias of +2.1 V is shown in Fig. 2. The amount of O₂ exposure is 0.1 L (1 L = 10^{−6} Torr s). Comparing Figs. 1 and 2, the bright sites observed in Fig. 2 are assigned to originate from the oxygen adsorption. On the other hand, only a few of the dark sites should be due to the oxygen exposure since the concentration, approximately 0.5% of the adatom sites, is almost the same as that on a clean surface. Taking into account the number of adatom sites in the area of the occupied state STM image, the number of the bright sites observed in Fig. 2 indicates that approximately 5% of the adatoms are affected by the 0.1-L O₂ exposure.

In most of the previous STM studies that observed the unoccupied states,^{13–18} not only bright sites, but also a large number of dark sites were observed upon oxygen adsorption. By combining the results of STS and a tight-binding calculation,¹³ the origin of these dark sites was reported to be the adatom whose dangling bond is saturated by an oxygen atom. This conclusion is supported by the recent combined STM and noncontact atomic force microscopy (NC-AFM) measurement,¹⁸ in which the dark sites observed in STM become bright in the NC-AFM image, suggesting the presence of adsorbates on top of the adatoms at those sites. In contrast to the previous STM studies,^{13–18} only a few dark sites, which originate from the oxygen adsorption, are observed in Fig. 2. The percentage of the dark sites was the same as that in Fig. 2 when imaging the surface using the unoccupied states with a tip bias of −2.1 V. Thus, the dif-

FIG. 3. Bias-dependent occupied state STM images of a 0.1-L O_2 -exposed $\text{Si}(111)-(7 \times 7)$ surface. The area corresponds to the area A displayed in Fig. 2. The tip biases are +2.1, +1.5, +0.8, and +0.5 V, and the corresponding tunneling currents are 0.15, 0.15, 0.1, and 0.05 nA, respectively. The two bright sites observed with a tip bias of +2.1 V are labeled A1 and A2.

ference between the previous and the present STM studies concerning the rather few dark sites in Fig. 2 is not due to the bias dependence of the contrast. The only reason that can explain the difference is that only a few dangling bonds are saturated by an oxygen atom in Fig. 2. Therefore, the small number of dark sites in Fig. 2 indicates the quite low adsorption probability of an oxygen atom to an on top site of an adatom at the initial stage of oxygen adsorption.

In order to consider the origin of the bright sites in Fig. 2 carefully, we have studied the 0.1-L O_2 -exposed $\text{Si}(111)-(7 \times 7)$ surface with different bias voltages. Figure 3 shows area A in Fig. 2, obtained with tip biases of +2.1, +1.5, +0.8, and +0.5 V. The tunneling currents were 0.15 nA for a tip biased at +2.1 and +1.5 V, 0.1 nA at +0.8 V, and 0.05 nA at +0.5 V. Two bright sites, labeled A1 and A2, are observed in the occupied state image obtained with a tip bias of +2.1 V. The A1 site disappears at a tip bias voltage lower than +1.5 V, and the A2 site is observed in all images. The observation of the A2 site with a tip bias of +0.5 V suggests the existence of a local density of states at the corresponding binding energy for this site.

In the previous studies,^{12,13} the dangling bond state of the adatom modified by an oxygen atom adsorbed into the back-

bond is reported to have a binding energy between 0.5 and 0.8 eV. Therefore, we propose that the origin of the A2 site is an adatom whose dangling bond state is shifted to a higher energy due to an oxygen atom inserted into its backbond. Considering the number of bright sites that are still observed at a tip bias of +0.5 V in the area shown in Fig. 2, we obtain the preference ratio of 2.6 for the faulted half of the unit cells compared to the unfaulted one and a preference ratio of 1.2 for corner adatoms compared to the center adatoms. These preference ratios are in good agreement with the ratios of bright sites reported previously for the unoccupied electronic states,¹³ whose origin is attributed to the modified dangling bond state. The agreement in preference ratios also supports the conclusion that the atomic oxygen is mostly adsorbed into the backbond of adatoms in Fig. 2. Taking into account that the number of bright sites is larger in the faulted half, the present results indicate the preferred adsorption site of atomic oxygen to be the backbond of an adatom of the faulted half at the initial stage of adsorption.

The disappearance of A1 at +1.5 V cannot be explained by a tip effect, like the movement of surface atoms, since it was bright using a tip bias of +2.1 V after the occupied state images of Fig. 3 were recorded. Thus, the bias dependence of A1 results from the electronic structure of this specific site. That is, the A1 site has a high local density of states only at binding energies of ≥ 2.1 eV. In the previous UPS study,¹² a metastable oxygen molecule adsorbed on top of an adatom, stabilized by an oxygen atom coadsorbed into the backbond, is reported to have the π_g orbital at a binding energy of 2.1 eV. As mentioned above, the adsorption of an oxygen atom into the backbond of an adatom should not show a bias-dependent brightness variation like the A1 site. For the oxygen atom adsorbed on top of an adatom, the Si-O bonding state has a binding energy of approximately 6 eV, and there is no density of states at a binding energy lower than that of the bonding state.^{3,12,13} The only configuration that is able to explain the bias dependence of the contrast of the A1 site is the metastable molecular species. Further, no site whose brightness shows the same bias dependence as that of the A1 site was observed after annealing the sample at 600 K, i.e., a temperature at which the molecular oxygen is reported to disappear.^{2,3,11,12} Hence, we conclude that the bright sites observed only with a tip bias of ≥ 2.1 eV are metastable molecular oxygen adsorbed on the $\text{Si}(111)-(7 \times 7)$ surface. Considering the total number of bright sites observed with a tip bias of +2.1 V and the number of bright sites that disappear at a bias of $\leq +1.5$ V, approximately 5% of the bright sites originate from the molecular oxygen. Moreover, the observation of 70% of the molecular oxygen at the corner adatom site of the faulted half indicates this site to be the preferred adsorption site of the metastable molecular species.

In the previous STM studies, although both Dujardin *et al.*¹⁹ and Martel *et al.*²¹ have observed the unoccupied state images using the same sample bias (+2.0 V) at room temperature, the assignments done for the molecular oxygen are completely different. Dujardin *et al.* assigned the bright sites as the metastable molecular oxygen, while Martel *et al.* assigned the dark sites, which are observed with a sample

biased at +2.0 V and turn bright after scanning the surface with a sample biased at +7.0 V, as the molecular species. The percentages of the molecular species in the total number of adatoms affected by the O₂ exposure are also different in these two studies; i.e., the percentage is more than 95% at a low exposure in the study of Dujardin *et al.* and approximately 7% in the study of Martel *et al.* To discuss the inconsistency between these two studies, we compare them with the present study. The percentage obtained by Dujardin *et al.* is completely different from that in the present study (5%), whereas the percentage obtained by Martel *et al.* is similar. The difference in percentage indicates that the origin of the bright sites, which are observed by Dujardin *et al.* in their unoccupied state image, should not be the molecular species. This agrees well with the NEXAFS study² and the theoretical calculation,²⁵ in which the molecular oxygen is stated to have no density of states at binding energy corresponding to the sample bias used by Dujardin *et al.*, i.e., 2 eV above the Fermi level. The similarity in percentage in the present study and the study of Martel *et al.* indicates that the same molecular species is observed in these two studies. In fact, Martel *et al.* suggested that the 7% of adatoms affected by the O₂ exposure correspond to the adsorption of a molecular oxygen on top of an adatom, which has an oxygen atom adsorbed into its backbond. However, not only the adsorption on top of an adatom but also another adsorption site was reported for the molecular species in the study of Martel *et al.*, i.e., the on top site of a rest atom. The adsorption of the molecular oxygen at the on top site of a rest atom is proposed by the observation of two dark neighboring adatom sites in the unoccupied state image, which result from an increase in the local tunneling barrier due to the oscillation of the molecular oxygen between the two adatoms. An increase in the local tunneling barrier should also affect the occupied state image, but no dark neighboring adatom sites were observed in the present study. In order to consider the adsorption of the molecular species on a rest atom more carefully, we have analyzed the bias-dependent occupied state STM images. The bias-dependent occupied state STM images show not only information on the electronic structure of the adatoms but also on the electronic structure of the rest atoms²⁶; e.g., the dangling bond states of the rest atoms are faintly observed in Fig. 3 with a tip bias of +0.8 V and clearly observed with tip biases of +1.5 and +2.1 V at the center of three adatoms. In the case that a molecular oxygen adsorbs on top of a rest atom, this rest atom site should be bright using a bias that corresponds to the binding energy of the molecular orbitals and dark with a lower bias. In this study, no rest atom site shows such bias dependence. Taking into account this result and the previous spectroscopic studies,^{2,12} which also reported the presence of only one adsorption site for the molecular oxygen, we conclude that any molecular species adsorbed on a rest atom should have a quite short lifetime and/or a very low adsorption probability.

Finally, since the molecular oxygen observed in the present study and the recent spectroscopic studies^{2,12} and one of the molecular species observed by Martel *et al.*²¹ interact with the adatom dangling bonds modified by the adsorption of an oxygen atom into the backbond, we discuss those dan-

FIG. 4. Bias-dependent occupied state STM images of the area B displayed in Fig. 2. The tip bias voltages are +2.1, +1.5, +0.8, and +0.5 V, and the corresponding tunneling currents are 0.15, 0.15, 0.1, and 0.05 nA, respectively. Among the five bright sites observed with a tip bias of +2.1 V, those that become darker than the unreacted adatoms at a bias of +0.5 V are labeled A2D, and those whose brightness is the same as the unreacted adatoms at +0.5 V are labeled A2B.

gling bond states, i.e., the bright sites that are still observed with a tip bias of ≤ 1.5 eV like the A2 sites in Fig. 3. The bias-dependent occupied state STM images of the area B in Fig. 2 are shown in Fig. 4. Five bright sites are observed in Fig. 4. Comparing the bias-dependent brightness of these sites, we recognize that all five sites are brighter than the unreacted adatoms with a tip bias of $\geq +0.8$ V. The observation with a tip biased at +0.8 V indicates that the origins of all five bright sites are the dangling bond states of adatoms with oxygen atoms inserted into their backbonds. Among the five bright sites, the two sites labeled A2D, which are located at the corner adatom site of the faulted half, become darker than those labeled A2B in the occupied state image obtained with a tip biased at +0.5 V. These A2D sites are also darker than the unreacted corner adatoms of the faulted half. A dark site observed in an STM image indicates a lower height of the atom and/or a lower density of states at the corresponding bias voltage. Taking into account that the height of an adatom with an oxygen atom adsorbed into its backbond is higher than an unreacted adatom,²⁵ the different brightness observed in Fig. 4 suggests a smaller density of states of the modified dangling bonds of A2D sites than those of A2B

sites and the unreacted adatom ones at a binding energy of 0.5 eV. Approximately 75% of the A2D sites are observed at the corner adatom site of the faulted half, and 70% of the molecular oxygen are observed at the corner adatom site of the faulted half. This agreement in percentage suggests the strong relation between the A2D sites and the adsorption site of the metastable molecular species. Moreover, since the modified dangling bond hybridizes with the antibonding π_g orbital of an oxygen molecule,^{2,12} a larger charge transfer from an adatom, originating from the larger density of states, would make the dissociation of the molecule easier. Therefore, we propose that the metastable molecular oxygen preferably adsorbs on the corner adatom site of the faulted half that has an oxygen atom adsorbed into the backbond due to its lower density of states, though we do not obtain the exact density of states of the modified dangling bonds at the A2D and A2B sites.

IV. CONCLUSION

We have investigated the initial stage of oxygen adsorption on a Si(111)-(7×7) surface at room temperature using

STM. The adatom sites affected by oxygen become brighter than the unreacted ones in the occupied state STM image obtained with a tip bias of +2.1 V. The higher number of bright sites observed in the faulted half indicates that this half is more reactive than the unfaulted half at the initial stage of oxidation. Among the bright sites, there are differences in the bias dependence of the brightness. Taking the previous UPS results into account,¹² we conclude that the bright sites observed only with a tip bias of $\geq +2.1$ V correspond to the molecular oxygen species. The preferred adsorption site of this metastable molecular oxygen is a corner adatom of the faulted half that has an oxygen atom adsorbed into its backbond.

ACKNOWLEDGMENTS

This work was financially supported by the Swedish Natural Science Research Council and the Carl Trygger Foundation (K.S.).

*Electronic address: sakamoto@surface.phys.tohoku.ac.jp

¹P. Bratu, K.L. Kompa, and U. Höfer, Phys. Rev. B **49**, 14 070 (1993).

²F. Matsui, H.W. Yeom, K. Amemiya, K. Tono, and T. Ohta, Phys. Rev. Lett. **85**, 630 (2000).

³U. Höfer, P. Morgen, W. Wurth, and E. Umbach, Phys. Rev. Lett. **55**, 2979 (1985); Phys. Rev. B **40**, 1130 (1989).

⁴P. Morgen, U. Höfer, W. Wurth, and E. Umbach, Phys. Rev. B **39**, 3720 (1989).

⁵G. Dujardin, G. Comtet, L. Hellner, T. Hirayama, M. Rose, L. Philippe, and M.J. Besnard-Ramage, Phys. Rev. Lett. **73**, 1727 (1994).

⁶G. Comtet *et al.*, Surf. Sci. **331-333**, 370 (1995).

⁷G. Comtet, L. Hellner, G. Dujardin, and M.F. Ramage, Surf. Sci. **352-354**, 315 (1996).

⁸K. Sakamoto, K. Nakatsuji, H. Daimon, T. Yonezawa, and S. Suga, Surf. Sci. **306**, 93 (1994).

⁹B. Lamontagne, D. Roy, R. Sporken, and R. Caudano, Prog. Surf. Sci. **50**, 315 (1995).

¹⁰K. Sakamoto, S. Suto, and W. Uchida, Surf. Sci. **357/358**, 514 (1996).

¹¹H. Ibach, H.D. Bruchmann, and H. Wagner, Appl. Phys. A: Solids Surf. **29**, 113 (1982).

¹²K. Sakamoto, S. Doi, Y. Ushimi, K. Ohno, H.W. Yeom, T. Ohta, S. Suto, and W. Uchida, Phys. Rev. B **60**, R8465 (1999).

¹³Ph. Avouris, I.-W. Lyo, and F. Bozso, J. Vac. Sci. Technol. B **9**, 424 (1991).

¹⁴F.M. Leibsle, A. Samsavar, and T.-C. Chiang, Phys. Rev. B **38**, 5780 (1988).

¹⁵H. Tokumoto, K. Miki, H. Murakami, H. Brando, M. Ono, and K. Kajimura, J. Vac. Sci. Technol. A **8**, 255 (1990).

¹⁶J.P. Pelz and R.H. Koch, J. Vac. Sci. Technol. B **9**, 775 (1991).

¹⁷Y. Ono, M. Tabe, and H. Kageshima, Phys. Rev. B **48**, 14 291 (1993).

¹⁸S. Kitamura, K. Suzuki, and M. Iwatsuki, Jpn. J. Appl. Phys., Part 1 **37**, 3765 (1998).

¹⁹G. Dujardin, A. Mayne, G. Comtet, L. Hellner, M. Jamet, E. Le Goff, and P. Millet, Phys. Rev. Lett. **76**, 3782 (1996).

²⁰I.-S. Hwang, R.-L. Lo, and T.T. Tsong, Phys. Rev. Lett. **78**, 4797 (1997); Surf. Sci. **399**, 173 (1998).

²¹R. Martel, Ph. Avouris, and I.-W. Lyo, Science **272**, 385 (1996).

²²F. Owman, Ph.D. thesis, Linköping University, 1996.

²³K. Takayanagi, Y. Tanishiro, M. Takahashi, and S. Takahashi, Surf. Sci. **164**, 367 (1985).

²⁴See, for example, Ph. Avouris and R. Wolkow, Phys. Rev. B **39**, 5091 (1989).

²⁵B. Schubert, Ph. Avouris, and R. Hoffmann, J. Chem. Phys. **98**, 7593 (1993).

²⁶R.J. Hamers, R.M. Tromp, and J.E. Demuth, Phys. Rev. Lett. **56**, 1972 (1986).