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Negative resist behavior of neutral sodium atoms deposited on self-assembled monolayers

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The authors report their initial studies of the negative resist behavior of neutral sodium atoms deposited on alkanethiol molecules during neutral atom lithographic processing. Their results show that neutral sodium atoms incident upon octadecanethiol, the longest molecule of the various alkanethiols among alkanethiol self-assembled monolayers (SAMs), formed the most robust negative resist during the patterning process and made high quality patterning profile. In order to interpret the nature of the surface interaction between neutral sodium atoms and SAMs, they examine the surface components using x-ray photoelectron spectroscopy, secondary ion mass spectroscopy, and rinse tests. Their results indicate that sodium neutral atoms do not chemically react with or physically damage the SAMs but rather accumulate on and possibly diffuse into the SAMs. © 2007 American Vacuum Society. [DOI: 10.1116/1.2431351]

I. INTRODUCTION

Demonstrations of focusing or deflecting atomic beams using standing-wave coherent optical fields have generated interest outside of the atomic cooling and trapping community in a new field called atomic nanofabrication (ANF).¹ ANF techniques can generally be classified as direct deposition (DD) or neutral atom lithography (NAL). The former refers to techniques of selectively depositing atoms onto a substrate, as one may do with dopants in semiconductor fabrication² or for construction of nanoscale magnetic devices through DD of ferromagnetic materials.³ NAL processing can be applied with organic materials or self-assembly molecules which cannot survive conventional lithography, printing methods, or lift-off techniques. Understandably, the atoms of choice in NAL have been those atoms that interact strongly with optical fields, resulting in large optical forces. These atoms include alkali metals [Cs (Refs. 4–7) and Na (Refs. 6–8)] and metastable noble gas atoms (He, Ne, and Ar).^{9–13} Most of these atoms have been shown to modify various types of molecular monolayers or self-assembled monolayers (SAMs) on several substrates including Au and SiO₂. The mechanism through which the etch resistivity is modified can be very different for various atomic species, internal energy, kinetic energy, or resist. While the physical mechanism leading to selective etch rates upon exposure to an incident beam of alkali metal atoms is still not well understood, the metastable noble gas atoms are believed to release their large internal energy (nearly 20 eV in the case of

He), which destroys the SAM backbone, leaving the region susceptible to chemical etching. In the case of alkali metal atoms from an effusive oven, there is only a small kinetic energy associated with the atoms (a few tens of meV); therefore the modification of the resist must derive from a different mechanism. One possibility is that a chemical reaction occurs between the highly reactive alkalis and the monolayer, perhaps involving the bond at the Au/SAM interface. Such a process is consistent with the positive tone resist behavior previously reported^{5–7} using Cs and alkanethiol SAM resists. Although briefly discussed,⁶ no detailed study of the interaction of Na atoms with SAM resists has been performed. While performing preliminary studies of NAL with an existing Na system, we found that the combination of Na atoms with alkanethiol SAMs in our process exhibited a negative resist behavior, in contrast with the positive resist behavior previously reported with Cs.

Much work has been done using self-assembled monolayers for various applications, including molecular electronics. This application is particularly relevant to the present study. The use of alkanethiols or other SAMs in molecular electronics requires interfacing with the molecules, most likely using metallic contacts on the ends of the molecules. One difficulty in the development of this technology has been the diffusion of contact metal atoms through the SAM.¹⁴ A recent time-of-flight secondary ion mass spectroscopy (SIMS) study¹⁵ indicated that potassium atoms form a layer on the top of the SAM that could potentially act as a chemical buffer on top of which a metal contact could be constructed, forming a component of a molecular electronic device. The properties of such a buffer layer are interesting to explore for other purposes, such as NAL.

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In this article, we present our studies aimed toward understanding the mechanism of negative resist behavior of neutral sodium atoms with alkanethiol SAMs on Au substrates exposed to a beam of neutral sodium atoms, using a physical contact mask. We have studied several alkanethiols of various chain lengths and the dosage requirements to obtain pattern transfer. In all cases, the exposed SAM acts as a negative tone resist, in which the regions of SAM exposed to the Na beam become more resistant to the chemical etchant. We have conducted x-ray photoelectron spectroscopy (XPS) and SIMS studies to help identify the observed patterning mechanism.

II. EXPERIMENT

In each of our experiments, we begin with a Au/Ti metal layer deposited on silicon by electron beam evaporation at $\sim 3 \times 10^{-7}$ Torr. We deposit the gold layer at a deposition rate of 0.3 \AA/s , with a total thickness of 30, 50, 80, or 100 nm over a 5 nm adhesion layer of titanium. We assembled eight different alkanethiol $[\text{HS}-(\text{CH}_2)_N-\text{CH}_3]$, N ranging from 5 to 17] SAMs, including hexanethiol, octanethiol, nonanethiol, decanethiol, dodecanethiol, tetradecanethiol, hexadecanethiol, and octadecanethiol on the Au/Ti surface, as follows. We prepare the self-assembly solutions by mixing the molecules with ethanol (1 mM) in an ultrasonic bath ($\sim 43 \text{ kHz}$) for 10 min. We place the gold metal samples in the SAM solution for at least 24 h, and subsequently rinse them in ethanol with 1 min ultrasonication. We dry the samples in an $85 \text{ }^\circ\text{C}$ oven for 20 min. We examine the SAMs formed on the Au/Ti surface by Fourier transform infrared spectroscopy to provide some measure of surface quality. After affixing a transmission electron microscopy copper grid (square crossed pattern of $5 \text{ }\mu\text{m}$ wires spaced by $50 \text{ }\mu\text{m}$) to serve as a physical mask, we insert the substrate into the atomic beam system for exposure to the sodium atomic beam.

The vacuum chamber in which we expose the samples to the atom beam is diffusion pumped (with a liquid nitrogen cold trap) and operates at a pressure of $\sim 1 \times 10^{-6}$ Torr. The Na beam originates in an effusive oven ($\sim 300 \text{ }^\circ\text{C}$) with a small aperture (1.7 mm diameter). A second small aperture (1.7 mm diameter, positioned 367 mm from the oven) forms a collimated atomic beam in the sample-exposure chamber of the vacuum system. The flux density of the Na beam is approximately $8.6 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$, as determined through optical weak-field absorption measurements, and we vary the exposure time, ranging from 15 to 120 min, in order to optimize the lithographic process. After exposure to the sodium beam, the sample is removed from the atomic beam system, the physical mask is removed, and the exposed surface is etched using a wet-chemical gold etchant (KI-I₂ based, Transene-type TFA) for 5 s. We then examine the quality of the transfer pattern on the substrate to determine which SAM is best suited as a NAL resist using an optical microscope, an atomic force microscope (AFM), and an XPS to analyze the elements on the Na/SAM surface.

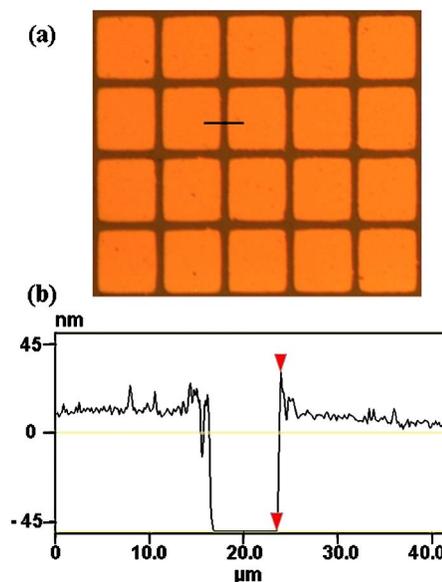


FIG. 1. Patterned Au regions after 60 minute sodium exposure on ODT/Au and subsequent etching. (a) Optical microscope image showing $50 \times 50 \text{ }\mu\text{m}^2$ Au patterns with $5 \text{ }\mu\text{m}$ spaces. (b) AFM line scan along line segment shown in image.

III. RESULT AND DISCUSSION

In our process, each of the eight Na exposed SAMs exhibits negative resist behavior, i.e., the gold layer remains in regions that are exposed to the sodium atoms, and is removed from regions that are not. This indicates that the SAMs themselves do not protect the Au surface from etchant. We observe that the octadecanethiol SAM (the longest molecule tested) results in the best pattern contrast with the cleanest separation between exposed and unexposed regions, with sharp transitions between these regions.

The time duration of the exposure of the SAMs to the sodium beam strongly affects the quality of the pattern transfer. For exposure times under 45 min, we are unable to discern any pattern transferred to the samples, i.e., the gold layer is removed from exposed and unexposed regions alike. For a 45 min exposure time a visible pattern remains; however, the exposed area of the sample is also partially etched. Exposure times of 60 min or more result in sufficient sodium dosage, and we observe fine negative tone features after the etching process. We show an example in Fig. 1(a), the optical microscope image of the processed gold pattern after a 60 min exposure of ODT to the sodium beam. Given that the surface density of alkanethiols is $\sim 5 \times 10^{14} \text{ cm}^{-2}$ (Refs. 5–7) and with the sodium flux density given above, a dosage of approximately 60 Na atoms per SAM molecule results from a 60 min exposure. This dosage represents the approximate number of atoms incident upon the surface, which could be significantly greater than the number of atoms that adhere to the surface.

One of the dominant factors in producing a uniform SAM layer is the surface morphology of the gold, as thin gold layers tend to develop in clusters rather than films of uniform thickness. SAMs grow unevenly on these clusters, resulting

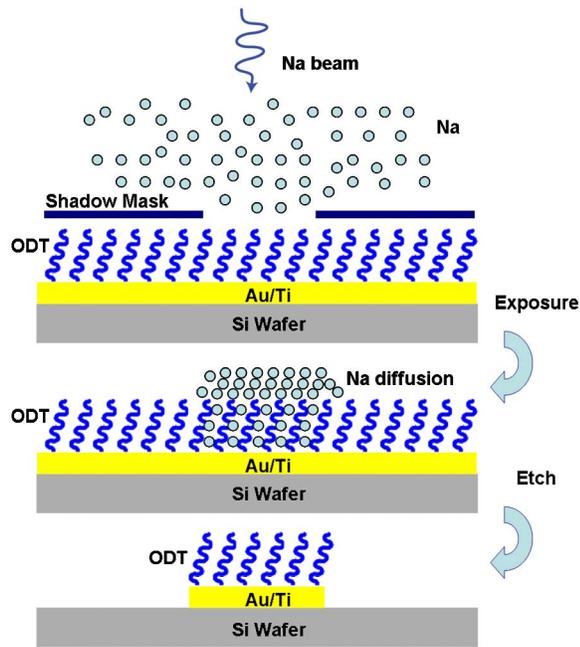


FIG. 2. Schematic diagram of negative resist action between sodium and the SAM on gold. After the chemical etch process, gold remains in regions exposed to sodium.

in degraded resist performance. To investigate the feasibility of sodium NAL to produce micron-scale patterns on a substrate we measured the width of the transition between the gold-coated surface and the etched surface, as well as the morphology of the gold/SAM surface after the etching process. We exposed several samples of varying gold thickness (30, 50, 80, and 100 nm) for 60 min each. Figure 1(a) shows an optical microscope image of a processed sample of ODT on an 80 nm thick Au layer showing $50 \times 50 \mu\text{m}^2$ patterns spaced by $5 \mu\text{m}$ gaps. Figure 1(b) shows the step profile taken on this sample with an AFM. The transition width between the etched area and nonetched area (SAM-Au) is ~ 330 nm with 80 nm gold thickness, and the rms surface roughness of the SAM-gold is ~ 2.2 nm on $4.6 \mu\text{m}^2$. We observed patterns of similar high quality for the other thicknesses of the gold layer we used. These results show that if the samples are exposed for a sufficient time (corresponding to about 60 sodium atoms per SAM molecule), any gold thickness can be etched and produce a fine pattern.

In order to investigate the reaction between Na atoms and the SAM, we exposed samples for 60 min and, before etching them, rinsed them in distilled water. When we rinsed the samples for 5 s, we observed some pattern transfer but with highly degraded contrast. During subsequent etching, the etchant penetrates the exposed area, resulting in a rough gold surface. Samples rinsed for more than 10 s showed no pattern transfer, indicating that the sodium is removed from the SAM surface, leaving the etch resistivity unchanged by the Na exposure. This result suggests that the Na does not chemically or physically alter the SAM but rather accumulates on the SAM surface (possibly diffusing into the SAM), thereby increasing the etch resistivity (Fig. 2).

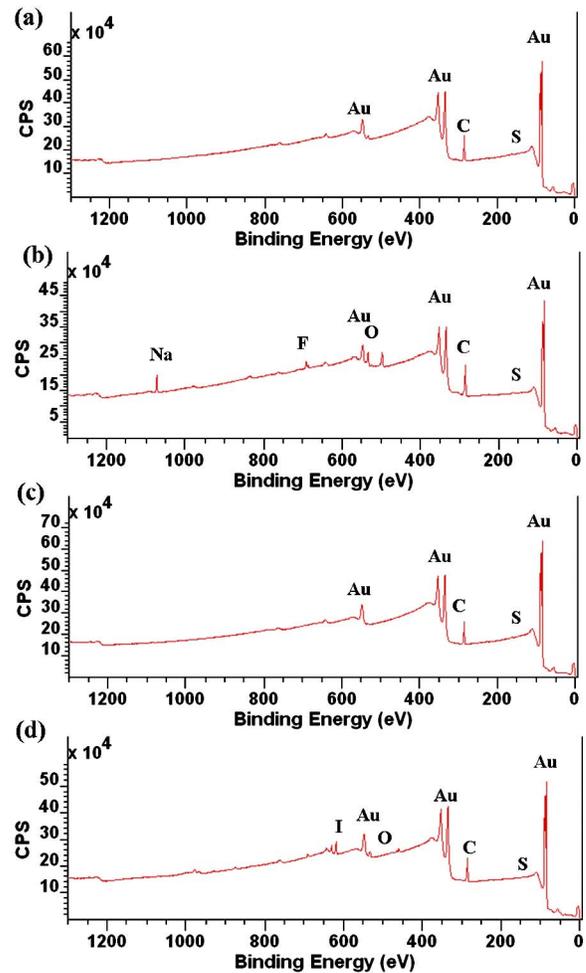


FIG. 3. XPS spectra: (a) an ODT/Au sample, not exposed to the sodium beam; (b) 60 minute sodium exposed ODT/Au sample; (c) 60 minute sodium exposed ODT/Au sample rinsed in distilled water for 10 s; and (d) 60 minute sodium exposed ODT/Au sample etched and rinsed.

We conducted an XPS analysis of the surface of several different substrates to study the chemical interaction and chemical composition of the surfaces. Four samples, each of which started with an ODT SAM grown atop a gold layer, differed as follows: (a) no further processing (ODT/Au), (b) a sample that we exposed to the sodium beam (Na/ODT/Au), (c) a sample that we exposed to the sodium beam and rinsed with distilled water (Na/ODT/Au), and (d) a sample that we exposed to the sodium beam, chemically etched, and rinsed with de-ionized water (etched/rinsed Na/ODT/Au). For this portion of the experiments, the samples were not masked. Figure 3(a) shows the XPS spectrum for the ODT/Au sample, which exhibits peaks corresponding to Au(4f, 84.2, 87.9 eV), S(2p, 164 eV), and C(1s, 285 eV) peaks. The XPS spectrum after sodium exposure [Fig. 3(b)] shows an intense Na peak (1s, 1072.6 eV). The line shape of Na 1s is a single state shape with a binding energy of 1072.17 eV, which indicates Na:O or Na:OH bonds. No addition peaks associated with Na:molecule interactions are observed, indicating a lack of chemical reactions with the molecule. We also observed impurities in the XPS spectra,

TABLE I. Atomic percentages of the elements found in each XPS spectrum: (a) an ODT/Au sample, not exposed to the sodium beam; (b) 60 min sodium exposed ODT/Au sample; (c) 60 min sodium exposed ODT/Au sample rinsed in distilled water for 10 s; and (d) 60 min sodium exposed ODT/Au sample etched and rinsed.

Elements	(a)	(b)	(c)	(d)
Au	35.4	0.71	32.6	30.7
C	63	2.55	65.7	62
S	1.6	0.03	1.7	0.7
Na		33.5		
O		52.48		4.3
F		10.68		
I				2.1
Ti				0.2

including oxygen ($1s$, 533 eV) and fluorine ($1s$, 686 eV) due to contamination of this sample. Figures 3(c) and 3(d) are the XPS spectra after rinsing and after etching, respectively. The sodium signal is clearly absent after rinsing or etching. We observe no evidence of chemical reaction between the sodium and ODT. Table I shows the atomic concentration of the elements of the four samples corresponding to Figs. 3(a)–3(d). The concentrations have been corrected for the cross sections of the respective elements and instrumental throughput. Following rinsing [Fig. 3(c)], the Na peak is no longer observed, and the S/Au and C/Au ratios are comparable to those observed prior to Na deposition. For the etched sample [Fig. 3(c)] the Na peak is no longer observed, and the S/Au and O/Au ratios are significantly reduced. During the course of the etching process, the Na overlayer and subsequently the ODT SAM are removed over time, as indicated by the XPS spectra and the observation of partial etching of the Au layer. A residual C peak is observed, which may correspond to other contaminants on the surface. The ratio of Na/C in the spectrum of Fig. 3(b) indicates approximately 230 Na atoms per ODT molecule, assuming that all of the observed carbon is within the ODT. However, attenuation of the C, S, and Au peaks in this case implies that the Na/C ratio observed in XPS significantly overestimates the actual ratio. Therefore, the XPS result generally agrees with a deposited thickness of 60 Na atoms or fewer per ODT molecule, inferred from deposition rate and time. This result suggests that sodium accumulates on top of the ODT, or perhaps diffuses into the ODT, and that this promotes the negative resist property. Iodine peaks ($3d$, 619 eV, 630.5 eV) in Fig. 3(d) are likely introduced from the gold etchant. The observation of relatively strong Au peaks in the spectra shown in Figs. 3(a) and 3(c) is attributed to the ~ 5 nm penetration depth of the x-ray beam, which is larger than the ~ 2 nm thickness of the ODT monolayer. For the spectra shown in Fig. 3(b), the C, S, and Au peaks are attenuated due to the presence of the relatively thick Na overlayer.

We examined two exposed samples using SIMS to study the chemical composition of the surfaces before and after etching. Of the two exposed samples, one was etched and subsequently rinsed in distilled water. Figure 4(a) shows that

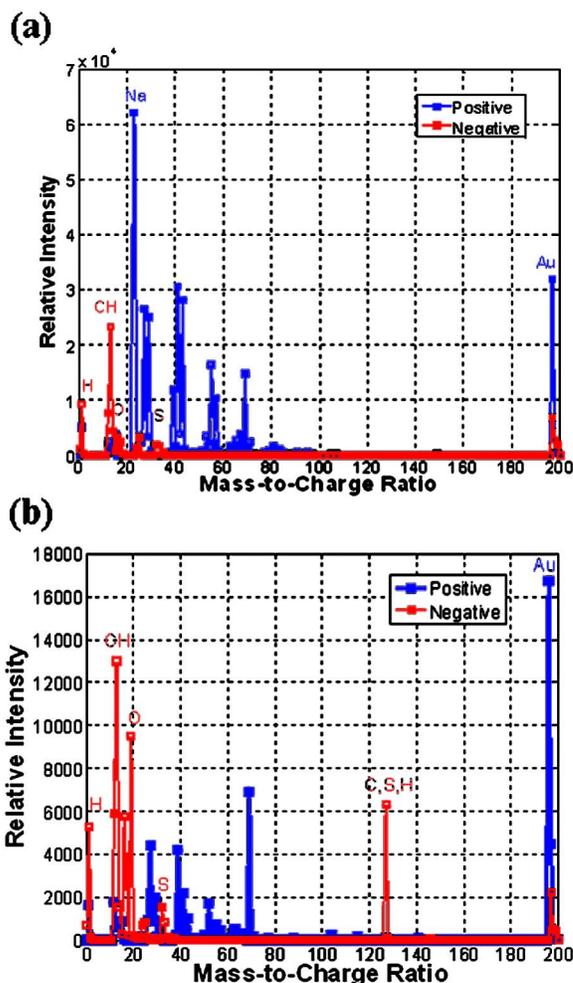


FIG. 4. SIMS spectra: (a) 60 minute sodium exposed sample showing sodium, ODT, and Au peaks and (b) rinsed samples after etching have ODT and Au peaks, but not sodium.

the exposed but not etched sample has Na (mass-to-charge ratio=23), C–H fragments from the ODT (1, 13, 32, and 127) and Au (196) peaks. The unexposed sample and the etched sample [shown in Fig. 4(b)] have C–H (ODT) and Au peaks, but no Na peak. In either spectrum, we identify the positive-ion fragment clusters of peaks centered around mass-to-charge ratios of 27, 41, 55, and 69 to be fragments of the alkanethiol chains, fragments which show no evidence of attached sodium atoms. Thus these spectra provide further evidence that the sodium atoms do not chemically bind to the ODT.

In an additional test, a sample without SAM was exposed to the Na beam and subsequently etched. The gold in the unexposed area was completely removed in the etching process, while the gold in the exposed areas was only partially removed. As a result, the contrast of the transferred pattern in the partially etched region was poor. There are at least two possible explanations for this partial pattern transfer. It may be possible that the sodium alone on the gold surface is responsible for the pattern transfer. It is also possible that some degree of contamination occurs in our vacuum system

or in transport prior to exposure. Because contamination lithography in NAL is usually performed in diffusion pumped systems,^{11,12} with longer exposure times and energetically different species (metastable noble gas atoms), we believe this to be at most a minor effect.

The behavior of the Na-SAM interaction in our process is consistent with previous studies of the interaction between alkanethiol SAMs and K or Na.^{15–17} It is interesting to note that in both of these studies, a low probability of sticking is observed when the atom impacts the SAM surface. Potassium atoms interacting with carboxylic acid ($-\text{CO}_2\text{H}$) or ester ($-\text{CO}_2\text{CH}_3$) terminated alkanethiols exhibit a much higher (~ 50 times) sticking probability. In that study the goal was to design a method of constructing metal contacts on the molecular surface while avoiding metal diffusion into the SAM. Such a buffer layer may also protect the SAM from a chemical gold etch, and we may reasonably expect pattern transfer for lower Na dosages and reduced exposure times using carboxylic acid or ester terminated SAMs. We are currently exploring this possibility.

IV. CONCLUSIONS

In summary, we have used a beam of neutral sodium to pattern self-assembled monolayers of alkanethiols on gold resulting in a negative tone pattern. To the best of our knowledge, this is the first report on the use of sodium as a negative resist for neutral atom lithography. The experiments indicate that the Na does not bond chemically with SAMs but rather accumulates on top of the SAM and possibly diffuses through the SAMs, acting as a protective resist against a wet-chemical gold etch solution. We found that when the Na dosage exceeds approximately 60 Na atoms per SAM molecule a robust negative resist is formed. With this protective layer in place, the roughness of the surface and thickness of metal were not dominant factors in the pattern transfer. Among the alkanethiol self-assembled monolayers tested, ODT (the longest chain tested) exhibited the best contrast. Nanoscale structures as produced in standing-wave lens experiments with sodium using the patterning mechanism described here remain to be demonstrated. However, we dem-

onstrate ~ 330 nm transitions with a gold layer 80 nm thick using neutral sodium atoms which suggests that production of smaller features may be possible. The current study focuses on Au but could be extended to direct patterning of other metal and oxide materials.

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¹D. Meschede and H. Metcalf, *J. Phys. D* **36**, R17 (2003).

²S. J. Rehse, R. W. McGowan, and S. A. Lee, *Appl. Phys. B: Lasers Opt.* **70**, 657 (2000).

³E. T. Slight, B. Smeets, R. C. M. Bosch, K. M. R. van der Stam, L. P. Maguire, R. E. Scholten, H. C. W. Beijerinck, and K. A. H. van Leeuwen, *Microelectron. Eng.* **67–68**, 664 (2003).

⁴F. Lison, H. J. Adams, D. Haubrich, M. Kreis, S. Nowak, and D. Meschede, *Appl. Phys. B: Lasers Opt.* **65**, 419 (1997).

⁵R. Younkin, K. K. Berggren, K. S. Johnson, M. Prentiss, D. C. Ralph, and G. M. Whitesides, *Appl. Phys. Lett.* **71**, 1261 (1997).

⁶K. K. Berggren *et al.*, *Adv. Mater. (Weinheim, Ger.)* **9**, 52 (1997).

⁷M. Kreis, F. Lison, D. Haubrich, D. Meschede, S. Nowak, T. Pfau, and J. Mlynek, *Appl. Phys. B: Lasers Opt.* **63**, 649 (1996).

⁸G. Timp, R. E. Behringer, D. M. Tennant, J. E. Cunningham, M. Prentiss, and K. K. Berggren, *Phys. Rev. Lett.* **69**, 1636 (1992).

⁹A. Bard *et al.*, *J. Vac. Sci. Technol. B* **15**, 1805 (1997).

¹⁰S. Nowak, T. Pfau, and J. Mlynek, *Appl. Phys. B: Lasers Opt.* **63**, 203 (1996).

¹¹S. J. Rehse, A. D. Glueck, S. A. Lee, A. B. Goulakov, C. S. Menoni, D. C. Ralph, K. S. Johnson, and M. Prentiss, *Appl. Phys. Lett.* **71**, 1427 (1997).

¹²K. S. Johnson *et al.*, *Appl. Phys. Lett.* **69**, 2773 (1996).

¹³K. K. Berggren *et al.*, *Science* **269**, 1255 (1995).

¹⁴B. C. Haynie, A. V. Walker, T. B. Tighe, D. L. Allara, and N. Winograd, *Appl. Surf. Sci.* **203**, 433 (2003).

¹⁵Z. Zhu, B. C. Haynie, and N. Winograd, *Appl. Surf. Sci.* **231–232**, 318 (2004).

¹⁶F. Balzer, K. Bammel, and H. G. Rubahn, *J. Chem. Phys.* **98**, 7625 (1993).

¹⁷K. Bammel, J. Ellis, and H. G. Rubahn, *Chem. Phys. Lett.* **201**, 101 (1993).