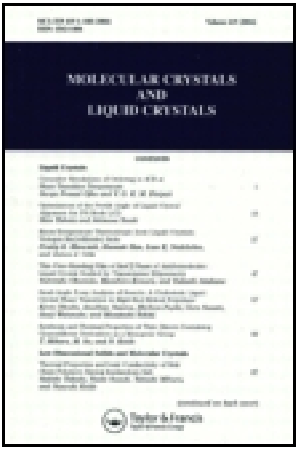

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Reversible Patterning of Ambient Carbon-Rich Deposits on a Gold Surface by Means of a Voltage-Biased Atomic Force Microscopy

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Reversible Patterning of Ambient Carbon-Rich Deposits on a Gold Surface by Means of a Voltage-Biased Atomic Force Microscopy

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We report on a reversible patterning of ambient carbon-rich deposits on a gold surface by using a voltage-biased atomic force microscope tip in air. This approach is capable of controlled writing, erasing, and rewriting of carbon-rich deposits with sizes in nanometer regime. Physical mechanism for this reversible patterning is proposed to be the current-induced electrochemical process.

Keywords reversible polymerization; electrochemical process; atomic force microscopy; nanofabrication; ambient carbonaceous deposit

INTRODUCTION

It is well known that exposure of a surface to an electron beam radiation in vacuum or air can lead to the formation of contamination film on the exposed area. This contamination film is conceived to be produced through electron beam induced polymerization of organic molecules that are adsorbed onto the surface. The sources of these organic molecules may include residual gas molecules such as hydrocarbon and carbon dioxide in ambient or vacuum environment and layers adsorbed onto the surface during sample preparation.

The use of focused electron beams generated from the tip of scanning tunneling microscope (STM) or secondary electron microscope (SEM) in vacuum has been shown to be effective in producing well-defined contamination deposits with nanometer sizes on the surface of films including gold, silicon, and silicon dioxide.[1] Contamination deposits written by these means have been used in a variety of applications such as an etch mask or a dip-pen nanolithography.[2] However, none of

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*Address for correspondence. e-mail: bmkim@sait.samsung.co.kr Fax: +82-31-280-9349 these studies were aimed at the erasing and rewriting of contamination deposits generated by electron beam.

In this study, we tested the possibility of using the voltage-biased AFM tip as a patterning tool for writing and erasing of contamination features on a gold film in ambient condition and as a tool for rewritable data storage. We provide evidences that it is possible to reversibly polymerize ambient gas species with nanometer scale controllability and that the mechanism underlying the reversible patterning is an electrochemical process.

EXPERIMENTAL

We used photolithography and liftoff to pattern 20-nm-thick evaporated Au films on a 300-nm-thick SiO_2 thermally grown on a Si(100) wafer. Each microfabricated Au pattern is consisted of a 10-um-wide strip and connected to large Au contact pads. After Au evaporation in a chamber under 10^{-8} Torr, the Au strips were transferred by liftoff using 10 min submerging in a 70 °C striping solution followed by 2-min rinse in flowing de-ionized water and N_2 blow dry. The samples were then mounted in a chip carrier, wire bonded, and loaded to a commercial AFM (Park Scientific Instruments, AutoProbe M5) system. AFM patterning and imaging were done under ambient conditions (with a relative humidity of ~ 45 % at 25 °C) using a contact-mode AFM equipped with 30 nm Ti-coated commercial Si cantilevers.

In the following, all voltages are quoted with the polarity of the tip side. In our experiments, the sample is grounded and the DC (constant or sweeping) voltages are applied to the tip. By applying a negative voltage to a fixed or a moving tip, a mound or a raised line was produced on a gold surface. We remark that no deposit of any kind was observable on a pristine gold film by using positive tip polarity up to 12 V. The samples are imaged with the same tip both before and after applying voltages.

RESULTS AND DISCUSSION

Figure 1(a) shows an AFM image of several mounds produced over a sweeping voltage range of –4V and -12V. As visible in the figure, this process rendered mounds in the

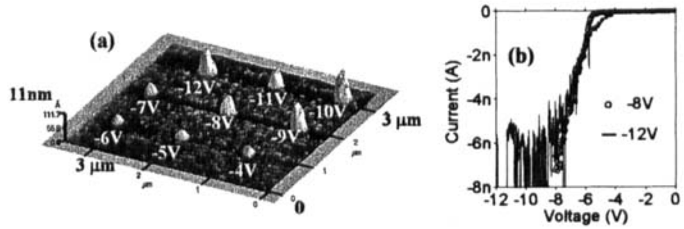

FIGURE 1. (a): AFM image of several mounds produced over a sweeping voltage range of –4 and –12V. (b): Two I-V curves obtained by measuring current flowing to the tip while applying sweeping voltages from 0 to –8 V and –12 V, respectively, during pattering two of the mounds in (a).

size range 0.1 um – 0.5 um in diameter and 4 nm - 11 nm high. In contrast to the report by Mamin *et al.*[3] where a threshold of ~3.5 V was observed for the mound formation under the field of a STM tip, we did not see a sharp threshold for the technique presented here. The threshold amplitude at which a given tip begins to produce mounds varied from under -3 to -9 V. Such a threshold behavior is illustrated in Fig. 1(b), which shows a typical current-voltage characteristic across the tip-sample junction during AFM patterning. The I-V curves in Fig. 1(b) were obtained by measuring a current flowing to the tip while applying sweeping voltages from 0 to –8 V and –12 V, respectively, during pattering two of the mounds in Fig. 1(a). We confirmed that a threshold voltage for a rapid current increases, such as the one seen around - 6 V in Fig. 1(b), marks the initiation of a mound formation. This observation indicates that the mound formation on a gold surface requires an electron transport across the patterning gap.

We were also able to create raised lines on a gold surface using multiple passes of a negatively biased scanning tip. Figure 2 shows a set of such lines produced over a constant voltage range of - 4 ~ - 8 V with - 2 V incremental step. The measured line width and height over this voltage range is between 80 nm – 300 nm and 3 nm –15 nm, respectively. Note that the probability of mound or line formation increases with increasing negative voltage. The observed size dependencies on the amplitude and the polarity of applied voltages indicate that a possible mechanism underlying the AFM patterning is an electrochemical process.

To better elucidate the physical mechanism, we analyzed the composition of patterned features with micro-Auger spectroscopy. Figure 3(b) shows a typical SEM image of a patterned feature. The ~ 2 um x 4 um monoclinic pattern in Fig. 3(b) was created by moving a −7 V tip orthogonal to a scan direction at a rate of 1um/s during

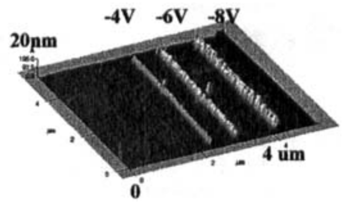

FIGURE 2. AFM image of a set of lines produced over a constant voltage range of − 4 ~ − 8 V with − 2 V incremental step.

patterning. As shown in the figure, patterned areas typically appeared much darker under SEM inspection that resembled contamination from background hydrocarbons. Auger electron spectroscopy measurements on the patterns revealed that the patterns are compositionally enriched with carbon. The spectra of P1 and P2 in Fig. 3(a) were

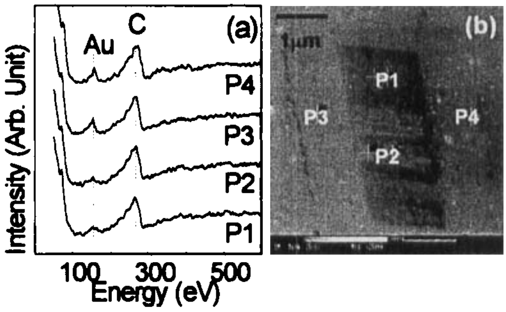

FIGURE 3. (a): Auger spectra of P1 and P2 in (a) were obtained from the patterned surface indicated respectively by P1 and P2 in (b). The spectra P3 and P4 in (a) were from bare Au surface of P3 and P4 in (b). (b): Typical SEM image of an AFM patterned feature on Au surface

obtained from the patterned surface indicated respectively by P1 and P2 in Fig. 3(b). The spectra P3 and P4 in Fig. 3(a) were obtained from the pristine Au surface indicated by P3 and P4 in Fig. 3(b). In both spectra, Au signal peaks at ~150 and carbon signal peak at ~280 can be seen. However, the Au peak intensity in spectra P1 and P2 is significantly reduced in comparison to that in spectra P3 and P4, since in region P1 and P2, the signal from the pristine Au film was masked by the carbon-rich feature produced via AFM patterning. The carbon detected away from the patterned site is likely due to the contamination during sample preparation and as it was exposed to room air for several days before Auger could be done.

The applicability of this technique for rewritable storage is demonstrated in Fig. 4. Shown in Fig. 4(a) is a 2 um x 3 um-monoclinic pattern written with a -6 V tip scanning at 1 um / s. The patterned area appears to be bright in the AFM image. It is noteworthy that the unpatterned area away from the carbon deposit exhibits a granular morphology of gold whereas such granularity is absent in the patterned area. By applying a +5 V stationary tip for 5 seconds over nine spots in the central region of the carbon feature in Fig. 4(a), we were able to erase a section of a 0.5 um x 0.7 um rectangular area as shown in Fig. 4(b). The granularity is revealed in the surface of the erased area. To get an information for how small an area can be erased, we applied a +5 V stationary tip for 5 seconds over three additional spots in the upper portion of the carbon deposit. This erasing sequence gave rise to three holes with the sizes in the range 100 nm diameter and 10 nm depth [Fig. 4(c)]. Fig. 4(d) is a result of a rewriting sequence where a 80 nm wide and 5 nm high mound was created with -6 V stationary tip applied for 5 seconds on a point in the center of the rectangularly erased area. This sort

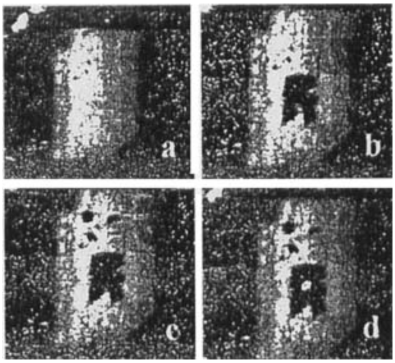

FIGURE 4. A typical example of rewritable data storage: (a) Written (-6V). (b) Large area erased. (c) Small area erased. (d) Bit rewritten.

of reversible patterning could be repeated for many times using a same tip without losing its ability for AFM imaging. Based on these findings, we surmise that a likely mechanism underlying the local erasing of carbon features is a current induced electrochemical dissociation and/or desorption of carbonaceous deposits.

Our interpretation that current induced chemical reaction occurring in the presence of ambient organic molecules may explain some previously reported results on STM surface and ballistic electron emission microscopy (BEEM) interface modification. In particular, we believe that what we are observing is the reversible interface and surface modification process recently seen by Hasagawa *et al.*[4] using combined STM and BEEM. They have suggested vacancy formation or charging effect at the interface as possible origins for the reversible modification at the interface. They have not, however, considered the reversible deposition of organic molecules from the ambient environment during patterning as an underlying mechanism. While other alternative explanations such as a field evaporation and desorbtion of atoms transferred from tip to surface or surface to tip are possible, a current-induced electrochemical deposition and dissociation of ambient carbon-rich film is an attractive picture to explain our observed reversible results.

CONCLUSION

We have demonstrated the controlled writing, erasing and rewriting of nanometer-scale carbon-rich deposits on a gold film from ambient gases using the voltage-biased AFM. Chemical analysis of these deposits shows them to be similar to deposits made using electron and ion beams, composed primarily of the carbon species. We think that the reversible patterning demonstrated here is not only applicable for integrated memory and data storage, but also can be employed for a large-scale maskless lithography.

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