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Nanometer Lithography on Silicon and Hydrogenated Amorphous Silicon with Low-Energy Electrons

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We report the local oxidation of hydrogen terminated silicon (Si) surfaces induced with the scanning-tunneling microscope (STM) operating in air and by a beam of free low-energy electrons. With STM, oxide lines were written in Si(100) and Si(110) and transferred into the substrate by wet etching. In case of Si(110) trenches with a width as small as 35 nm and a depth of 300 nm were made. The same process has also successfully been applied to the patterning of hydrogenated amorphous silicon (a-Si:H) thin films. We demonstrate the fabrication of metallic 'nanowires' using a-Si:H as resist layer. With regard to the process of oxidation, it is found that the oxide written with STM is apparently not proportional to the electron current, in contrast to results obtained with a beam of free electrons in an oxygen gas-environment. The dose needed to remove the hydrogen was determined as a function of electron energy. This dose is minimal for 100 eV electrons amounting to 4 mC/cm².

1. Introduction

Further downscaling of device dimensions demands new technologies capable of fabricating nanometer structures. The approach of applying low-energy electrons to e-beam lithography is promising because proximity exposure due to secondary electrons is reduced or eliminated. A prototype process is the local oxidation of hydrogen passivated Si, as first demonstrated by Dagata et al. on Si(111) using the scanning-tunneling microscope STM in air [1]. Snow et al. applied this process to Si(100) and demonstrated that the oxide pattern can serve as a mask for wet etching [2].

With the present work we extend this process to the fabrication of deep nanometer-wide trenches anisotropically etched into Si(110) and to thin layers of hydrogenated amorphous silicon (a-Si:H) serving as resist. In addition, the efficiency of the process is studied in air as well as in a vacuum setup in which a beam of free electrons is available.

2. Experimental

The oxidation was studied on three different types of substrates: A) Si(100) and Si(110) substrates (10 mΩcm), B) thin films (25–40 nm) of a-Si:H (10²⁰ cm⁻³) deposited on undoped Si(100),

and, C) a-Si:H thin films similar to B but now deposited on a thin metal film (10 nm TaIr) DC-sputtered on undoped Si(100). Substrate A and B are used to investigate the writing and etching on crystalline and amorphous silicon, respectively. Substrate C served to demonstrate the feasibility to pattern a metallic thin film into 'nanowires' using the process of local electron-induced oxidation. Prior to writing, the substrates were dipped in dilute hydrofluoric acid (10 %) for the hydrogen passivation, followed by rinsing in deionized water [3].

In the STM mechanically prepared Pt/Rd tips were used and the STM was operated in the constant-current mode using tunneling currents $I_t = 1 - 100$ pA. Oxide lines were written with negative tip-substrate voltages $U_t = -2.4$ to -4.0 V with writing speeds in the range 0.1–1 μm/s. After writing, we sometimes imaged the oxide pattern with STM now applying positive U_t ($U_t = 2$ V, $I_t = 5$ pA). Imaging is possible, because the rate of oxidation with positive U_t is found to be much lower than with negative U_t .

Following the exposure, the pattern is transferred into the substrate by wet etching. To fabricate narrow and deep structures into crystalline Si it is necessary to have a very selective and anisotropic etch liquid. We have tried three liq-

uids that are known to etch Si anisotropically: KOH [4], EDP [5], and TMAH [6]. Best results were obtained with 40 wt. % TMAH which etches Si with a selectivity as high as 10^4 with respect to silicon-oxide. With this etching solution, low etching rates desirable for nanostructures are possible without the drawback of residues as it is the case for EDP. Because of this, TMAH has been used throughout this work. Typical etching rates are 600 nm/min at 75 °C for Si(110) and 200 nm/min at 65 °C for a-Si:H. Anisotropically etched structures are bounded by {111} crystal planes. This limits the achievable depth of trenches for Si(100). Deeper trenches can be fabricated in Si(110) if the oxide lines are written along the $[11\bar{2}]$ direction [4].

The electron beam induced oxidation of Si was studied in a vacuum chamber (base pressure 10^{-10} mbar), where a sample can be exposed to e-beam radiation. During exposure the chamber can be floated which oxygen gas at pressures ranging from 10^{-8} to 10^{-3} mbar. Here, we report the measurement of the exposure dose required to remove the hydrogen from the Si surface. This is done without adding oxygen gas to the vacuum chamber. After exposing different locations on the sample for different electron doses and energies, the sample is removed from the vacuum chamber. If hydrogen has been desorbed oxidation will occur spontaneously, forming a thin oxide layer. The sample is then etched with TMAH at 75 °C for 10 seconds. This etches about 100 nm of Si, but does not etch through the formed native oxide layer. Inspection of the etched sample with the scanning-electron microscope (SEM) reveals the exposure requirements.

3. Results and Discussion

3.1. STM Lithography

In this section we present representative structures fabricated on the substrates A-C using STM lithography. All the images shown are obtained with a scanning-electron microscope (SEM) on the final etched structures.

Fig. 1 shows a line pattern oriented along the $[11\bar{2}]$ direction on Si(110). The lines are ≈ 75 nm wide separated by ≈ 60 nm wide trenches 300 nm

Figure 1. SEM picture of lines obtained on Si(110) after etching with TMAH.

in depth. Up to now, the smallest 300 nm deep trench has been 35 nm wide corresponding to an aspect ratio of ≈ 10 . Writing many structures re-

Figure 2. Attempt to write a circle by STM lithography.

veals some problems characteristic to STM lithography. Fig. 2 shows a curved line obtained on Si(100). Here we attempted to write a large circle. As can be seen, the obtained line pattern is not closed. This effect, known as creep, is caused by the piezoelectric elements used to displace the tip. The response of a piezoelectric element to a voltage change has two contributions: an instantaneous displacement and a time dependent component which decays very slowly (creep). We have tried to correct for this, but a general compensation algorithm has not yet been found. Fig. 3 demonstrates an artefact. The text shown

Figure 3. Figure showing effect of STM double tip in (a).

in (a) has obviously been written twice. Single exposure results in the text shown in (b). The double exposure is due to a tip having two asperities that are simultaneously in 'contact' with the substrate during writing (double tip). In this example, the asperities are laterally displaced by 500 nm. In Fig. 3 weaker lines are seen (arrow) connecting the three words. These lines appear at positions where exposure should ideally be absent. The text pattern is written with a negative tip-substrate voltage $U_t < -2$ V. In order to move the tip from one pattern to the next one without exposing the substrate, U_t is set positive to 2 V. Fig. 3 demonstrates that also at positive U_t there can be some residual exposure. This we have found to be strongly dependent on the tip for reasons that are not known at present. We point out that there are tips which do not produce any structure for $U_t \gtrsim 2$ V. The lithography process described is limited to crystalline Si. The application potential of local oxidation can greatly be expanded if thin films of amorphous hydrogenated silicon (a-Si:H) can be structured. These films are stable in air, can be passivated with hydrogen and evaporated on almost any substrate. With the STM we successfully oxidized the surface of 30 nm a-Si:H films evaporated on Si sub-

Figure 4. Lines processed on a ≈ 30 nm amorphous Si film on Si(100).

strates and used the oxide as an etching mask. Fig. 4 shows a SEM picture of 40 nm lines after etching the a-Si:H. A drawback of a-Si:H is that it

Figure 5. Successful patterning of a metal film into submicron wires using hydrogenated amorphous-silicon as resist.

etches isotropically. This results in a partial underetching of the oxide mask. To demonstrate the patterning of a metal film, a layer of a-Si:H is used as resist on top of a thin 10 nm TaIr metal film. After processing the silicon layer, the pattern is transferred into the metal film by sputter-etching using Ar ions. We succeeded in the fabrication of metallic wires using this approach. An example is shown in the SEM picture of Fig. 5.

3.2. Process of Oxidation

Figure 6. The minimal electron exposure-dose to remove the hydrogen from the silicon surface as a function of kinetic energy of the electrons.

STM images of oxide lines written by STM using different parameters have been compared. The oxidation is found to be more pronounced for larger negative writing voltages with a threshold of $U_t \approx -2$ V. In a simple picture, the electrons from the tip induce the removal of the hydrogen from the surface leading to oxidation. Increasing the current is expected to increase the efficiency of the process. It is found however that the current hardly influences the oxidation ($I_t = 1 - 100$ pA) while the writing speed does [3]. This is in contrast to experiments in UHV where a clear dose dependence is found. It has been proposed recently, that the oxidation process in air may result from an electrochemical reaction taking place between the STM tip and the substrate [7].

Because of its relevance to low-energy e-beam lithography we show in Fig. 6 the minimal dose required to desorb the hydrogen from the Si(100) surface as a function of kinetic energy of the incident electrons E_p . This result has been obtained in UHV. For $E_p \approx 100$ eV this dose is minimal amounting to ≈ 4 mC/cm². This should be compared with the dose of typically 1 C/cm² used for air STM experiments. At lower energies, the dose increases strongly. Assuming that the hydrogen removal is caused by a direct interaction

of the incident electrons with the Si-H bond via an inelastic scattering process, the efficiency of this process is expected to increase with decreasing energy, down to electron energies comparable to typical binding energies. Just the opposite is seen in Fig. 6. We think that even at these low energies the hydrogen removal from the silicon surface is primarily caused by secondary electrons emitted from the surface. This is supported by noting that the yield y – the number of emitted secondary electrons per incident electron with energy E_p – is proportional to E_p , for $E_p < 100$ eV [8]. If our conclusion is correct, the minimal feature size in electron-beam lithography using electrons with low energies of order ≈ 100 eV is limited by secondary electrons (assuming a point electron source). One should bear in mind, however, that the effective lateral spreading of the primary beam due to scattering and secondary electron emission can be very small at low energies enabling to achieve a resolution of a few nanometers. The true challenge is to build an electron-optics giving a one nanometer electron-beam spot for 100 eV electrons.

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