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Laser direct writing of oxide structures on hydrogen-passivated silicon surfaces

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A focused laser beam has been used to induce oxidation of hydrogen-passivated silicon. The scanning laser beam removes the hydrogen passivation locally from the silicon surface, which immediately oxidizes in air. The process has been studied as a function of power density and excitation wavelength on amorphous and crystalline silicon surfaces in order to determine the depassivation mechanism. The minimum linewidth achieved is about 450 nm using writing speeds of up to 100 mm/s. The process is fully compatible with local oxidation of silicon by scanning probe lithography. Wafer-scale patterns can be generated by laser direct oxidation and complemented with nanometer resolution by scanning probe techniques. The combined micro- and nanoscale pattern can be transferred to the silicon in a single etching step by either wet or dry etching techniques. © *1996 American Institute of Physics.* [S0003-6951(96)00646-8]

Hydrogen-passivated silicon surfaces have attracted much interest because of their well-defined state and bulk-like surface reconstruction. They are used as starting layers for epitaxial growth and as resist layers for nanolithographic techniques, such as scanning tunneling,[1,2] atomic force,[3–5] and—most recently—scanning near-field optical lithography.[6] This is because hydrogen-passivated silicon layers have ideal resist properties such as the possibility of depositing ultrathin layers (<10 nm) with good step coverage and high sensitivity to electrical currents and fields for pattern definition. The scanning probe techniques are based on the probe-induced removal of the hydrogen passivation and the subsequent oxidation of the exposed surface in air or another oxidizing atmosphere. The resulting oxide pattern is used as an etch mask.

One of the major problems of scanning probe lithography is the connection of the produced nanostructures to the macroscopic world. Both the fabrication of large patterns and the alignment of nanostructures to large patterns pose severe challenges to the serial scanning probe techniques with their often limited scan ranges, slow scan speeds, and low tolerance to surface steps.

Here, we report a new approach to optically generate wafer-scale oxide patterns on hydrogen-passivated silicon surfaces and analyze the physical mechanisms involved. The oxide patterns are detected by an atomic force microscope, which can be used to add features with sub-100 nm resolution to the optically defined pattern. A single etching step transfers the combined pattern into the silicon, which is a considerable simplification compared to approaches which require two different lithographic steps to define micro- and nanostructures, and which avoids the problem of scanning over steep edges during nanostructuring on photoresist-defined microstructures.[7]

The laser direct-write system used for the oxidation experiments consists of a continuous-wave argon ion laser with UV option, beam conditioning and focusing optics, and high-resolution direct-current motor stages with internal encoders for sample translation.[8] The system is designed to achieve minimum spot sizes and high-resolution positioning (~100 nm repeatability) over large areas (100×100 mm^2). Typical achievable spot sizes are around 500 nm for 458 nm light. To generate a pattern, the beam is modulated on the fly using direct positioning pulses from the stages, while the substrate is translated with speeds of up to 100 mm/s.

For the experiments on amorphous silicon, substrates are thermally oxidized to a thickness of about 50 nm and covered with a boron-doped amorphous silicon (*a*-Si) layer, 10–100 nm thick and produced by direct current magnetron sputtering (Fig. 1). Substrates for the experiments on crystalline silicon are not pretreated. Before direct writing, the silicon samples are dipped in 5% hydrofluoric acid for 60 s in order to strip the native oxide and passivate the surface. After exposure to laser light in air, the samples are either etched in 25% potassium hydroxide (KOH) at room temperature for 30–270 s, depending on the thickness of the *a*-Si layer, or transferred to an atomic force microscope (AFM) for further processing or for investigation of the grown oxide.

Exposure of the hydrogen-passivated silicon surfaces to laser light results in an oxide with a thickness comparable to
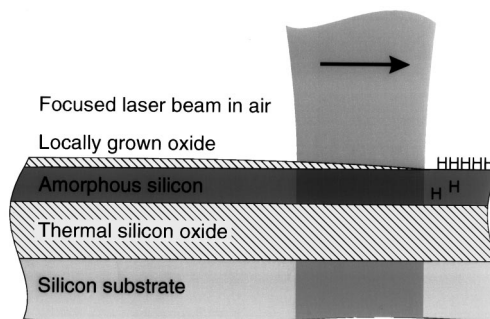

FIG. 1. Schematic of the laser direct write process. The *a*-Si layer is depassivated by the focused laser beam and oxidized after exposure to air.
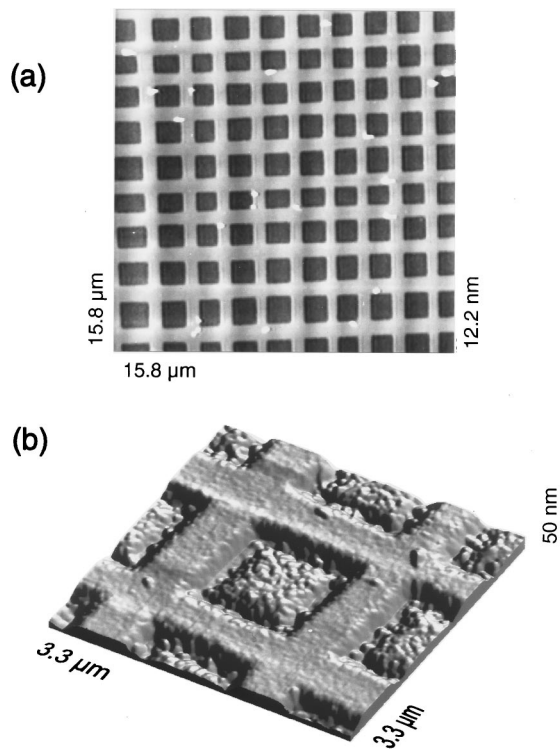
FIG. 2. AFM images of a-Si structures after KOH etching using a laser-generated oxide mask. (a) Large area pattern in 10 nm thick a-Si on oxide, (b) close-up for 100 nm thick a-Si on oxide.

FIG. 3. Minimum power density for the optical desorption of hydrogen from the surface of a 10 nm thick a-Si layer as a function of exposure time for different laser wavelengths. The data point for 351 nm laser light is taken from Ref. 9. The inset shows the wavelength dependence of the minimum power density for two different exposure times.

a native oxide, which suggests that hydrogen is desorbed by a photoinduced process similar to electrically induced desorption, followed by the oxidation of the depassivated surface. Optical desorption of hydrogen has first been reported by Kramer *et al.* for long exposure of passivated crystalline silicon to a static laser interference pattern.[9] The optical desorption of hydrogen requires a minimum power density, which depends on substrate absorption, laser wavelength, and exposure time.

We have made quantitative desorption experiments on 10 nm thick a-Si on oxide by determining the threshold conditions for writing a test pattern (Fig. 2). Figure 3 shows the minimum power density required for the formation of an oxide layer sufficient to mask 10 nm of a-Si for KOH etching, as a function of exposure time. The corresponding minimum energy dose ranges from 0.02 to 20 kJ/cm^2 with the lowest dose required for the shortest exposure time. For all investigated wavelengths (351, 458, 488, and 514 nm), the minimum power density remains constant for almost 3 orders of magnitude for exposure times between 0.1 and 100 ms. Above 100 ms, the minimum power density drops nearly linearly with exposure time, i.e., the minimum energy density is constant. For comparison, the dose and exposure time used by Kramer *et al.*[9] is included in the figure. The change of slope in the time dependence suggests that more than one desorption mechanism is involved in the hydrogen desorption process.

Three mechanisms which are known to cause efficient hydrogen removal are thermal desorption, desorption by optically induced excess carriers, and direct optical interactions with surface atom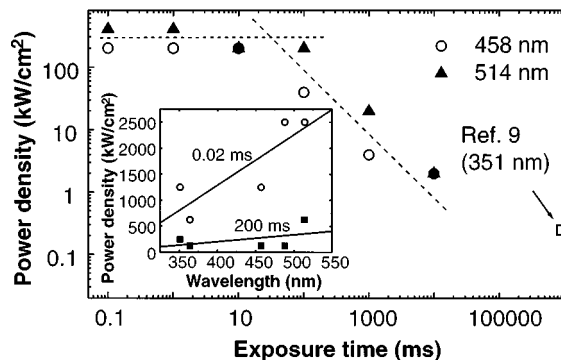s and molecules. Possible direct optical processes include destabilization and dissociation of Si–H bonds[9] and excitation of adsorbed OH groups.[10]

In order to estimate the effect of thermal desorption, the laser-induced maximum temperature rise has been calculated assuming a Gaussian beam profile and cooling by three-dimensional conduction into the substrate.[11] The resulting temperature rise ranges from less than 1 K to almost 400 K for power densities between 2 and 200 kW/cm^2, respectively.

For short exposure times, the required power density is high enough to heat the substrate to the point of efficient thermal desorption of hydrogen at about 700 K. In this regime, the writing speed can be increased to more than 100 mm/s using a spot size of about 0.5 μm, allowing fast large-area direct patterning. Linewidths of down to 450 nm and line edges with radii of curvature of less than 20 nm have been measured by AFM imaging after KOH etching. The observed wavelength dependence of the minimum power density needed for patterning is similar to the wavelength dependence of the absorption coefficient of a-Si (Fig. 3, inset), in agreement with a thermally stimulated process.

At low power densities and long exposure times the calculated temperature rise is negligible. The mechanism in this regime is believed to be either an excited carrier process or a direct optical process. Both mechanisms can explain the enhanced hydrogen desorption observed for higher photon energies: The wavelength dependence can be a result of the absorption edge of a-Si for excited-carrier-induced desorption,[12] and for direct optical dissociation the energy barrier can be in the range of 2.5 eV. No resonancelike behavior is observed in the wavelength dependence of the desorption process (Fig. 3, inset).

The compatibility of the laser direct write technique with STM and AFM lithography is demonstrated in Fig. 4. The images show two narrow leads connected to contact pads with a 2 μm gap, written by laser direct oxidation. This gap has been bridged with a nanowire written by AFM lithography after detecting and aligning to the laser-generated oxide pattern. The AFM is run in contact mode in air using a titanium-coated silicon nitride tip and applying a voltage between -5 V and -10 V for oxidation.[13] The entire process of defining contact pads and wires with an area of about 1 mm^2 by laser direct writing and the 200 nm wide and 2 μm
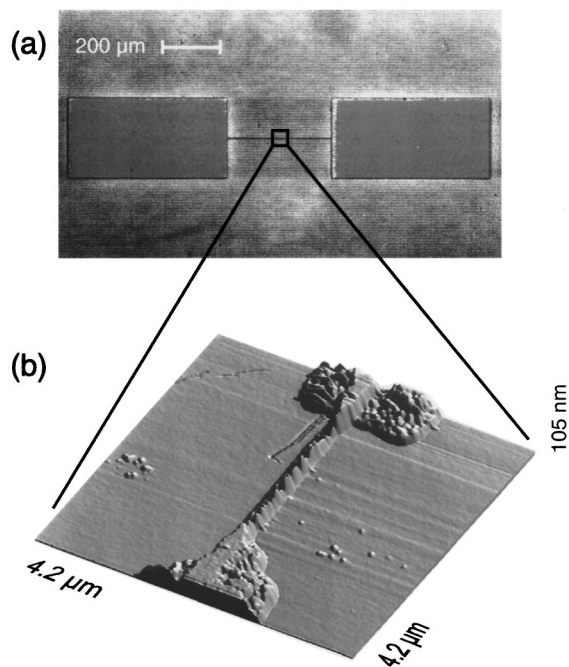
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FIG. 4. (a) Optical microscope image of laser-defined contact pads with leads. (b) AFM image of an AFM-written nanowire bridging a 2 μm gap between the leads from the contact pads, demonstrating the compatibility of AFM and laser oxidation. The oxide pattern has been used as a mask for KOH etching of a 100 nm thick a-Si layer, which is completely removed in the unoxidized areas.

long nanowire by AFM writing can be completed in less than 1/2 h, which is fast enough to avoid substantial deterioration of the passivated surface in air.

Based on our results, several improvements and variations can be envisaged. While the locally grown native oxide in the presented experiments is only a moderate masking material, the oxide quality can be improved by desorbing hydrogen in a controlled oxidizing atmosphere at elevated temperatures. Using the optical desorption process for projection of masks would require very powerful or focused light sources since the required power density is very high compared to standard photoresist exposure. However, modified mask aligners or wafer steppers with increased UV illumination or focused light arrangements could reach the required power densities and make this process interesting for industrial applications. In particular, laser-based wafer steppers can deliver higher power densities in the UV range, which will drastically reduce exposure times as shown in Fig. 3. Sputtered a-Si layers can easily be deposited with a good step coverage and high uniformity on structured substrates, which is very interesting for pattern definition on bulk micromachined devices. Furthermore, a-Si can be patterned to a very high resolution, since it has an atomic granularity and a well-defined chemical composition.

In conclusion, we have shown that it is possible to locally oxidize hydrogen-passivated silicon surfaces by exposure to light with a photon energy above 2.5 eV. Different mechanisms play a role in the desorption process as a function of power density. Thermal desorption appears to be the dominant mechanism in the high power density range. This has been used to directly write patterns with scan speeds of up to 100 mm/s with submicron resolution. The power density needed for desorption decreases with increasing exposure time above 100 ms, which indicates a different desorption mechanism in this regime. For low power densities, the induced temperature increase is negligible, and direct optical or induced carrier processes are possible mechanisms. We show that laser direct writing of oxide structures is a particularly convenient complementary technique to scanning probe lithography on passivated surfaces, since it allows fabrication of large-scale connections to nanometer-scale circuitry, without increasing the number of processing steps.

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