Electron beam induced carbon deposition used as a negative resist for selective porous silicon formation

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Abstract

The present work describes direct porous silicon patterning based on electron-beam induced carbon deposition used as a mask against pore formation on Si. Under ideal conditions the C-deposits act as a negative resist to suppress completely and selectively the formation of light emitting porous Si at treated locations. Carbon patterns were written at different electron doses on p-type Si(100) surfaces. Subsequently by contamination writing in a scanning electron microscope the silicon surface was porosified by galvanostatic experiments in a 20% HF solution. The carbon masks as well as the etched surface were characterized by scanning electron microscopy and Raman spectroscopy. The selectivity of the technique depends on several factors such as the electron dose during masking and the electrochemical parameters. Under conditions typical for porous silicon formation, already a relatively low electron dose is sufficient to achieve the desired mask effect to produce patterned porous silicon structures.

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1. Introduction

Nanomaterials have in recent years attracted a great deal of scientific interest. On the one hand interest focuses on possibilities to prepare and study materials with novel properties which are encountered when nanosize dimensions are approached. On the other hand a major thrust for shrinking dimensions originates from the micro-electronic and microsystems fields with a continuous demand for a higher degree of smaller devices, system integration and system diversification. This implies that the classical microelectronic materials or newly integrated materials need to be microstructured to obtain a higher functionality. To achieve sub-μm resolution a wide range of processes have been studied including lithographic techniques essentially based on exposure of resists to photons, X-rays and electron-beams (e-beam). More recently, direct patterning of surfaces has also been investigated using focussed ion beams (FIBs) [1–3] or atomic force microscopy [4,5].
In the context of functional semiconductor surfaces the discovery of interesting optical properties from porous silicon such as visible room temperature photoluminescence (PL) [6] and electroluminescence has recently opened new perspectives for Si-based integrated circuits [7]. These remarkable optical properties of porous Si can be attributed to the quantum confinement responsible for a change in the energy levels compared to bulk Si [6,8,9]. A key step in the fabrication of integrated optical/electronic circuits using porous Si is the incorporation of the material into a circuit design directly on the single-crystal Si substrate with well-defined dimensions and satisfactory resolution. Formation of porous Si patterns have traditionally been investigated using lithographic processes. Alternatively, direct processes such as photoanodic etching and photocathodic protection reactions [10], doping-induced selective porous silicon [11] and amorphization-controlled selective porous Si [12] have been used. Recent work has also demonstrated that the selective formation of visible light emitting porous Si can be achieved by FIB sensitization of n-Si followed by a selective electrochemical treatment [3,13].

In technological applications e-beam lithography is mainly used to fabricate photolithographic masks [14]. In research, however, also exploratory direct processes are investigated e.g. to generate ultrasmall linewidths on both Si and SiO₂ [15–19]. E-beam induced deposition reactions have also been studied to create 3D nanostructures in the 1–100 nm range [20–22]. In this approach, the e-beam activates gaseous precursor species introduced into the vacuum chamber of the e-beam instrument leading to solid deposits at the irradiated surface. Typically the precursor vapor species that are used are metalorganic compounds or, more simply, the residual hydrocarbons from the pump oil. In the latter case, (so called contamination writing), the hydrocarbon molecules adsorbed on the surface react under e-beam to form an amorphous structure of carbon, more specifically a layer of diamond-like carbon (DLC) with electrical and mechanical properties comparable to diamond [23,24].

Such contamination writing has been applied as a mask using ion milling [25] or recently to achieve high definition patterning of semiconductor surfaces for subsequent metal electrodeposition [26]. In this previous work we showed how to use C-masks produced by contamination writing in a scanning electron microscope (SEM) to suppress completely and selectively metal electrodeposition at treated surface locations. The key of the approach is the fact that in comparison with the resistivity of the Si the DLC layer behaves as an insulator and thus can block the electrodeposition of the metal. It was demonstrated that carbon deposits of the order of only 1 nm thickness can be sufficient to achieve a negative resist effect, i.e. to block the electrodeposition of metals on a Si(1 0 0) surface completely and selectively [27,28]. Within the present work we investigate the feasibility of using such C-patterns on Si(1 0 0) as a mask for the electrochemical fabrication of porous Si patterns.

2. Experimental

Experiments were carried out on p-type Si(1 0 0) wafers with a resistivity of 8–13 Ω cm. The samples were then degreased by sonicating in acetone, isopropanol and methanol, rinsed with deionized water and dried in an argon stream.

To achieve e-beam induced deposition of the C-patterns, the samples were irradiated in a JEOL 6400 SEM. Deposition of carbon occurs in vacuum systems pumped with untrapped oil diffusion pumps. This contamination resist is formed when the e-beam “cracks” the thin layer of hydrocarbon molecules condensed at the sample surface. As a result, a cone of resist builds up at the point of impact of the e-beam. The rate of buildup can be increased by increasing the partial pressure of hydrocarbons with a local source of vapor or by increasing the electron dose. Single e-beam deflection and patterning was carried out using Elphy Quantum lithography software. On each sample two series of seven rectangles of 50 × 5 μm were deposited with increasing electron doses: 0.1 × 10³, 0.5 × 10³, 1.0 × 10³, 1.5 × 10³, 2.0 × 10³, 2.5 × 10³ and 3.0 × 10³ μC/cm². In one series the spacing between the rectangles was 10 μm in the other series it was 20 μm. During the deposition the pressure of the chamber was 10⁻⁴ Pa, the
voltage was set to 20 kV and the probe current was 50 pA. Chemical characterization of C-deposits was carried out by Auger electron spectroscopy (AES) using the C peak at 270 eV and the Si peak at 1621 eV. AES spectra were acquired on a Perkin Elmer 670 AES spectrometer. To gain additional information on the nature of the carbon films Raman spectroscopy measurements were performed. The spectra were obtained with a HR 800 integrated Raman system from Jobin Yvon using an Ar⁺ line ($\lambda = 487.98$ nm) at room temperature.

After the e-beam treatment, contact to the Si samples was established by smearing InGa eutectic on the backside of the samples. The samples were pressed against an O-ring of an electrochemical cell leaving a surface of 0.79 cm² to the electrolyte. The electrochemical set-up consisted of a conventional three-electrode configuration with a platinum gauze as a counter electrode and a Haber–Luggin capillary with a Ag/AgCl (1 M KCl) electrode as a reference electrode. Electrochemical experiments were carried out using a Jaissle potentiostat–galvanostat (IMP 88PC–100 V). The electrolyte was a 20% HF solution prepared from reagent grade chemicals and deionized water. Porosification of C-patterned Si samples was carried out by galvanostatic experiment; different anodic currents $10^{-5}, 10^{-4}$ and $10^{-3}$ A/cm² were applied for 5 min. PL measurements were performed at room temperature with an Ar⁺ 514.5 nm excitation line using the Raman detection equipment previously described.

3. Results and discussion

3.1. Deposition of the C-masks

Fig. 1a shows a SEM image of C-patterns e-beam deposited on a Si surface. It is apparent that in the two series the seven rectangles are distinctly visible. Patterns are more visible for the higher electron doses indicating that the thickness of the carbon layer increases continuously with increasing e-beam exposure. It is noteworthy that the patterns deposited with $0.1 \times 10^{13}$ μC/cm² e-beam dose do not appear on the SEM. In order to characterize in more detail the carbon distribution over the surface, scanning AES maps for C (Fig. 1b) and Si (Fig. 1c) were taken from Fig. 1a. In both cases the light areas correspond to the presence of C and Si respectively. From these images, it is observed that the intensities for C and Si are complementary, i.e. the intensities of the Si are lower where the C signal indicates the presence of C on the surface. Therefore the presence of C at the irradiated locations is demonstrated and these results confirm also that the higher the electron dose, the thicker C layers are deposited. It can be pointed out that the AES images in Fig. 1b and c appear blurred compared with the corresponding SEM image as the lateral resolution of the scanning AES is significantly lower than for the SEM. Further analysis of the C-patterns was carried out by Raman spectroscopy. Fig. 1d shows the Raman spectrum obtained from C deposit and has also been discussed in Ref. [29]. In the region between 1200 and 1800 cm⁻¹ a broad peak centered around 1550 cm⁻¹ (G-band) and the presence of the so-called shoulder at around 1350 cm⁻¹ (D-band) typical for amorphous DLC films are observed [24,30,31]. These results indicate that the sp³- and sp²-bonded C is incorporated in the e-beam deposited material; thus these findings can explain the insulator behavior previously observed [26–28].

3.2. Pore formation

In order to study the C-mask effect under porosification conditions, galvanostatic experiments in 20% HF electrolyte were performed on samples carrying the C-patterns. It has been reported that porosification of p-type Si occurs at anodic current densities higher than $10^{-5}$ A/cm² [6]. Then, various anodic current densities higher than $10^{-5}$ A/cm² have been used during this work. Fig. 2 shows an optical image of the C-patterned sample after an electrochemical treatment with $10^{-5}$ A/cm² for 5 min. The unexposed area (surrounding the patterns) exhibits interference colors ranging from red to brown. These interference colors are typical of thin porous silicon layers. From the image it is clearly apparent that some of the C-deposits are completely or partially attacked. This means that the surface is modified
except at the locations carrying the C-patterns if a sufficient electron dose is used for the carbon deposition. C-patterns, deposited using electron doses higher than $1.0 \times 10^3 \mu\text{C/cm}^2$, do not suffer from any etching. Therefore, it is evident that C-deposits produced with a dose higher than $1.0 \times 10^3 \mu\text{C/cm}^2$ can act as a mask to the electrochemical etching in HF solution and thus constitute a negative resist blocking completely and selectively the pore formation. It has to be pointed out that this threshold value of $1.0 \times 10^3 \mu\text{C/cm}^2$ represents a very low electron dose and therefore a very thin carbon layer is sufficient to block the electrochemical etching reactions. For comparison, a typical dose of 0.1–1 C/cm$^2$ is required to produce a carbon mask for ion etching [32]. This result demonstrates that extremely thin carbon layers lead to a satisfactory mask effect. Indeed, as our previous work have demonstrated, C-deposits in the order of less than 1 nm thickness are sufficient to block completely electrodeposition reactions [26,27]. C-deposited patterns created with lower electron doses varying between 0.1 $\times 10^3$ and $1.0 \times 10^3 \mu\text{C/cm}^2$ do not show a complete

Fig. 1. SEM image of two series of seven C-patterns deposited with an increasing electron dose from the left to the right (a), scanning AES maps for C (b) and Si (c). Raman spectrum ($\lambda = 487.98$ nm) obtained from C deposit (see Ref. [29]) (d).
masking effect. The C-pattern deposited with the lowest dose has entirely disappeared indicating a total lack of masking efficiency.

In order to investigate in more detail the morphology of the pores a SEM image of the part of the surface carrying the 10 μm spaced C-patterns was taken (Fig. 3a). The presence of seven rectangles corresponding to the treated surface locations confirms the previous observations. In comparison with the C-protected areas, the surface is clearly rough due to the presence of a highly porous structure. It can be also noticed that the higher the electron dose the better resolution at the edge of the C-deposits. In order to study in more detail the interface C-masked surface/porosified surface a picture centred at the edge of the 3 × 10^3 μC/cm² exposed pattern was taken at a higher magnification (Fig. 3b). The picture shows clearly two distinct regions separated by a sharp boundary. The smooth part is the C-covered area. The porous structure shows a typical pore size of approximately 90 nm whereas absolutely no pores or signs of etching are visible within the carbon area. Additional information about structure and selectivity were also obtained through the analysis of the cross-section related to the 3.0 × 10^3 μC/cm² exposed pattern. This etched cross-section was obtained by focused ion beam (FEI 800 × P) with a Ga⁺ beam at 30 kV. The ion image taken at 45° (Fig. 3c) reveals that a layer of approximately 0.75 μm in thickness has grown selectively at the both sides of the exposed area. From this picture it is also deduced that the growth of porous Si is very homogeneous and isotropic at the mask edges compared with other masking techniques that produce selective porous Si including the use of masks like organic photoresists, thick silicon dioxide and silicon nitride [33,34] where frequent inhomogeneities of mask edges occur. It is particularly remarkable that in our case absolutely no lateral undercutting of the layer below the protected surface is observed and hence the porous layer shows no cracks. For these advantages and simplicity this technique opens new perspectives to create selective porous Si with a very high lateral resolution.

The resist effect can be explained in terms of resistivity of the C-deposit. As it has been already found according to Raman measurements, C formed under the e-beam consists mainly of C sp³- and sp²-bonded amorphous C. This composition confers to the deposit electrical properties close to diamond [24], therefore the C-deposit behaves as an insulator and can suppress electrochemical reactions. As this suppression of reactivity also works for electrodeposition reactions, it is clear that the C-deposit must possess insulating properties [26–28]. Furthermore this material seems to persist in the harsh HF environment, i.e. it is stable against chemical dissolution.

For each sample, the PL properties of porous Si layers were preliminary assessed using a UV light source. For all the conditions used the porous Si formed exhibited a strong red visible luminescence except for the C-treated locations. In order to investigate in more detail the optical selectivity of such C-patterns, a series of PL measurements was performed. Fig. 4a shows an example of a PL spectrum acquired within the C-deposit 3.0 × 10^3 μC/cm² exposed and another spectrum acquired close to the deposit. Compared with the flat PL response within the C-masked area, the spectrum taken next to the pattern exhibits a large peak in the red region between 600 and 850 nm with a
maximum at approximately 700 nm, typical for porous Si. To verify the selectivity of the optical response a luminescence scan ($\lambda = 514.53$ nm) across the C-patterns was performed using the maximum PL intensity. Fig. 4b shows the optical image of the C-treated sample after electrochemical treatment and the corresponding luminescence across the C-patterns. It is apparent that the PL intensity of locations protected by the C-mask deposited for electron doses higher than $1 \times 10^3 \mu$C/cm$^2$ is zero and thus, no light emitting structure is present within the C-patterned areas. In contrast, the intensity between these C-deposits reach a high value corresponding to the maximum PL response. It can also be pointed out that the PL intensity within C-deposited for electron doses lower than $1 \times 10^3 \mu$C/cm$^2$ is in same range as the rest of the untreated surface confirming that a sufficient masking effect is not achieved.

During this work the C-mask effect under different porosification conditions was also studied. A series of galvanostatic experiments was performed on samples carrying the same C-patterns as described above. Fig. 5a and b show the SEM images of the C-pattern deposited with a $3.0 \times 10^3 \mu$C/cm$^2$ electron dose treated under modified electrochemical conditions that are $10^{-4}$ and $10^{-3}$ A/cm$^2$ anodic polarization in HF for 5 min. From Fig. 5a the mask effect is total, absolutely no signs of etching is visible within the protected area.
Compared with Fig. 3a and b the structure of the porous silicon is slightly different: the unexposed surface is also completely porosified but a typical pore size in the 0.5 μm range is obtained. It has to be mentioned that under these electrochemical conditions, a higher electron dose is required to achieve a complete blocking of etching; in this case for electron doses lower than $2.0 \times 10^3 \, \mu\text{C/cm}^2$ no satisfactory mask effect was observed. Under more severe conditions (Fig. 5b) again the C-deposit can act as a negative resist. It is apparent that the surface morphology is different from Figs. 3a and 5b: a lot of fine porous structure is visible except at the C-mask location. For these conditions, an

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Fig. 4. PL spectra acquired within and close to the C-deposit $3.0 \times 10^3 \, \mu\text{C/cm}^2$ exposed (a). Compared with the flat PL response within the C-masked area, the spectrum taken next to the pattern exhibits a large peak in the red region between 600 and 850 nm with a maximum at approximately 700 nm, typical for porous Si. Optical image of the C-treated sample after electrochemical treatment and the corresponding luminescence scan ($\lambda = 514.53 \, \text{nm}$) across the C-patterns (b). It is apparent that the PL intensity of locations protected by the C-mask fabricated for electron doses higher than $1.0 \times 10^3 \, \mu\text{C/cm}^2$ is close to zero and thus, no light emitting porous structure is present within the C-patterned areas.
A selective electrochemical formation of porous Si. The approach is based on producing masks by e-beam induced decomposition of residual hydrocarbon molecules present in a SEM chamber to form a C-rich deposit. The electrical resistivity of this C-deposit is very high due to a high amount of amorphous C and thus this material can act as an insulator and suppress completely and selectively electrochemical reactions such as in this work the formation of pores in Si. There is a threshold dose that is required to achieve a total masking effect. The results clearly show that selective formation of light emitting porous Si can be achieved by this technique with an excellent lateral resolution. This negative lithographic process depends strongly on C-deposition as well as electrochemical parameters. It has been found that a very thin C layer can be sufficient to block completely etching reactions. The very low electron dose required to achieve the negative resist effect as well as the excellent resolution obtained at the edges of the C-deposits open new perspectives not only for selective light emitting porous Si but also, more generally, for the direct patterning of surfaces.

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