Factors in Electrochemical Nanostructure Fabrication Using Electron-Beam Induced Carbon Masking

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The present work investigates the fabrication of Au nanostructures using the masking effect of carbon patterns deposited by the electron-beam (E-beam) of a scanning electron microscope for electrochemical reactions. E-beam induced deposition is based on the decomposition of residual hydrocarbon species (molecules from the pump oil) to create a solid deposit at the point of impact of the E-beam. Subsequently, such E-beam deposited matter is used to completely block the electrochemical deposition of Au in the nanometer scale. In this work, several factors affecting the resolution of the process are studied. Electrochemical conditions as well as control of the E-beam C-mask are investigated to optimize the lateral resolution of the process. Especially, it is demonstrated that the beam energy used for depositing the C-mask plays a crucial role in fabricating Au nanostructures in the sub-50 nm range.

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Miniaturization of materials in the nanometer scale has attracted the entire semiconductor industry as well as a large community of scientists and engineers because of the explosion of potential applications leading to significant, fundamentally new advances in different fields including physics, chemistry, materials science, and biology. To date, optical lithography is the main technique used for the integrated circuit (IC) industry, but the current strategies employed are blocked by optical diffraction. Thus, new approaches and alternative techniques have been developed to downsize the dimensions of structures, see, e.g., reports on the LIGA process, microcontact printing, and proximal probe lithography. For a large overview see Ref. 7.

Particle beam lithography and especially electron-beam lithography (EBL) are approaches that have been widely investigated to produce structures in the sub-100 nm range. The process steps of such resist-based techniques are essentially the same as those used for photolithography, except that the pattern on the resist is obtained by scanning the focused particle beam directly across the surface. Due to a very high resolution, EBL is mainly used to produce masks and prototype nanoelectronic device fabrication.

Electron-beam-induced deposition (EBID) is an approach using a beam of electrons to produce 3D nanostructures. This single-step direct writing technique is carried out in a conventional or modified scanning electron microscope (SEM) or transmission electron microscope (TEM). The principle is based on the focused electron-beam-induced decomposition of adsorbed precursor molecules introduced into the vacuum chamber of the E-beam instrument. If the precursor species used are metallicorganic compounds, the materials obtained show a nanocomposite structure with metal nanocrystals of variable size embedded in an amorphous matrix. The main constituents of the matrix are C and the metal present in the precursor molecules. Due to the combination of high resolution and 3D structuring, EBID is highly appreciated in the field of exploratory nanodevice fabrication and has recently moved towards applications for production of conducting lines, X-ray mask repair, photonic crystals, and a wide range of devices. When the precursor species used are only the residual hydrocarbon molecules issued from pump oil, a carbongeous deposit is obtained at the E-beam treated locations. In previous work, the chemical composition of such an E-beam deposited compounds has been investigated by Auger electron spectroscopy (AES). The derivative of the Auger spectrum obtained from this material was compared with Auger spectra obtained from pure graphite and chemical vapor deposition (CVD) deposited diamond which were taken as references. According to the literature, it has been found that E-beam deposited material is carbon-containing. More specifically, the spectrum reveals the presence of sp²- and sp³-bonded C. This amorphous structure of C, so-called diamond-like carbon (DLC) exhibits electrical properties comparable to diamond. Recently, it has been reported that such E-beam induced C deposit can be used as a negative resist for electrochemical reactions, i.e., it has been demonstrated that E-beam C deposit in the nanometer range of thickness can block completely and selectively electrodeposition of metals on Si surfaces as well as the electrochemical etching of Si. This C masking effect has also been employed to fabricate TiO₂ structures on Ti surfaces.

In this work, several factors such as the electrochemical conditions and E-beam parameters affecting the resolution of the process are investigated in order to fabricate nanostructures. It is demonstrated that under optimized electrochemical conditions the lateral resolution of the process strongly depends on the E-beam parameters and especially the beam energy used for depositing the C-mask.

Experimental

Experiments were carried out on n-type Si(100) wafers with a resistivity of 5-8 Ω cm. The wafers were cleaved to samples of 1.2 × 1.2 cm and were degreased by subsequently sonicating in acetone, isopropanol, methanol, and rinsed with deionized water. The samples were dipped in 1% HF for 30 s to remove the air-formed native oxide layer and to H terminate the Si surface. Finally, the samples were rinsed in deionized water and dried under a nitrogen stream. InGa eutectic (99.99%) was smeared on the back side of the samples to establish an ohmic contact.

Samples were patterned using a JEOl 6400 thermionic emission SEM equipped with the lithography software Elphy Quantum and a beam blanker provided by Raith GmbH. On each of the sample array of 10 lines, 50 μm in length, equidistantly spaced (1.5 μm) were deposited with increasing electron doses, nC/cm² with 0.1 ≪ n ≪ 1. During the deposition the pressure of the chamber was 10⁻⁴ Pa, the working distance was set to 10 mm, and the probe current was constant and equal to 10 pA at 5 keV and 50 pA at 20 keV. Then, samples were pressed against a 10 nm diameter O-ring of an electrochemical cell which consisted of a conventional three-electrodes configuration. Platinum gauze served as a counter electrode, and a Ag/AgCl electrode (E = 236.3 mV vs. SHE) was used as a reference electrode. Deposition of Au was achieved by potentiostatic experiments in a 10 mM KAu(CN)₂ + 1 M KCl electrolyte (pH 8.5). The electrochemical cell was always placed in a black box in order to avoid any noncontrolled photoelectrochemical effects.

Chemical characterization of the E-beam deposited was carried out by AES using the C peak at 270 eV and the Si peak at 1621 eV. AES spectra were acquired on a Perkin-Elmer 670 spectrometer. Topog-
raphy of the samples after E-beam treatments was obtained by atomic force microscopy (AFM) using Pico SPM from Molecular Imaging driven by a Nanoscope E controller from Digital Instruments used in the contact mode and equipped with a 100 μm piezoscanner and an ultrasharp silicon tip.

Capacitance measurements were performed with a Zahner IM6 setup (Zahner Elektrik, Kronach, Germany). A potential ramp was applied in the anodic direction for n-type Si with a step of 65 mV and the amplitude of perturbation was 10 mV. The Mott-Schottky plots were recorded in the frequency range of 1 kHz. Current transients and potentiostatic experiments were carried out with an EG&G PAR 273A model.

Results and Discussion

Deposition of the C mask.—In order to characterize the C distribution over the surface, AES line scans were acquired as a function of the distance perpendicular to the two series of C lines. Figures 1a and b show the scanning AES experiments performed on a Si sample carrying the ten C lines written with 5 and 20 keV beam energy, respectively. In both cases, the results clearly indicate the presence of the ten C lines. It has to be pointed out that the C and Si intensities are complementary, i.e., the intensity of the Si peaks decreases when the intensity of the Auger C peaks increases suggesting that the amount of C increases with increasing electron dose.

Figures 2a and b show the height and width of the C lines taken from the corresponding AFM profiles (Fig. 2c and d). The height value was taken at the maximum and the linewidth was defined as the full width at half-maximum (fwhm) of the Gaussian cross section. In all cases, the C linewidth tends to reach a limiting value for electron doses higher than 0.4 C/cm² whereas lineheight increases with increasing electron dose suggesting that a high aspect ratio is achieved through the E-beam-induced deposition technique. In agreement with the fact that the higher the beam energy, the smaller the spot size, it is apparent that the widths of the deposits increased with decreasing beam energy. It can be pointed out that the line- widths are much broader than the estimated probes size (less than 100 nm), which confirms that the deposition of carbon is determined not only by the primary E-beam size, but also by the distribution of the scattering electrons emitted from the substrate.

Electrochemical investigations.—The description of the interface according to the model of Gerischer can be used to determine the range of potential for electrochemical metal deposition as well as to describe the mechanism involved.36 First, the determination of the flatband potential (Vfb) is required to obtain the schematic representation of the interface according to the model of Gerischer. The flatband potential corresponds with the potential of zero excess charge in the space-charge layer of the semiconductor. It can be determined by an extrapolation of the so-called Mott-Schottky plot of the capacity measurements, namely a plot of 1/C² vs. the externally applied voltage.37,38 The Mott-Schottky relation is given by Eq. 1

\[ \frac{1}{C^2} = \frac{2}{\varepsilon e \varepsilon_0 N_D} (V - V_{fb}) \]  

where V is the applied voltage, N_D the doping concentration, \( \varepsilon \) is the dielectric constant in the direction normal to the surface, and \( \varepsilon_0 = 8.854 \times 10^{-14} \text{ F/cm} \) is the permittivity of the vacuum. The extrapolation to 1/C² → 0 yields the flatband potential, and from the slope where the plot is linear the dopant concentration N_D is deduced. It is found from the Mott-Schottky plot shown in Fig. 3 that V_{fb} is approximately -1.0 V (Ag/AgCl) and N_D = 10¹⁵ cm⁻³. According to Eq. 2

\[ E_{c,s} = qV_{fb} + kT \ln \left( \frac{N_c}{N_D} \right) \]  

where the effective density of states in the conduction band is \( N_c = 2.8 \times 10^{19} \text{ cm}^{-3} \), the lower level of the conduction band at the semiconductor surface (\( E_{c,s} \)) is -1.23 V (Ag/AgCl) with respect to the flatband potential. Since the Fermi level of the semiconductor has to be adjusted to the equilibrium potential of the electrolyte (\( V_{eq} = -0.71 \text{ vs. Ag/AgCl at pH 8.5} \)), the interfaces are in a depletion situation as shown in Fig. 4a. This schematic representation of the interface under open circuit potential (OCP) condition is deduced from Eq. 3

\[ E_{c,b} - E_F = kT \ln \left( \frac{N_c^0}{N_D} \right) \]
where the lower level of the conduction band in the bulk semiconductor \(E_{c,b}\) is approximately \(-0.95\) V (Ag/AgCl) and the upper level of the valence band in the bulk semiconductor \(E_{v,b}\) is approximately \(0.15\) V (Ag/AgCl). The equilibrium potential is about \(-0.71\) V (Ag/AgCl), so that the energy levels of the Au acceptor states are expected to overlap only with the conduction band. As there is no overlap of Au acceptor states with the valence band, electrons cannot be transferred from the semiconductor to the solution. Consequently, Au deposition cannot be observed under OCP condition. According to the model of Gerischer, deposition of Au occurs at higher cathodic voltages than \(V_{FB}\), i.e., when the interface is in an accumulation situation. Theoretically, cathodic voltages higher than \(V_{FB} = -1.0\) V (Ag/AgCl) are required to initiate the transfer of electrons from the electrolyte to the semiconductor via a conduction band mechanism. The accumulation situation is illustrated in Fig. 4b where an external voltage of \(-1.6\) V vs. Ag/AgCl is applied.

In order to verify if deposition of Au on the Si surface is achieved for cathodic potentials, higher than \(V_{FB}\), a series of current transients at potentials in the range \(-1.0\) V (Ag/AgCl) to \(-1.6\) V (Ag/AgCl) was carried out (Fig. 5). In accordance with the values of potentials obtained from the model of Gerischer, a significant cathodic current leading to Au deposition is only observed for applied potentials higher than \(V_{FB}\), whereas no Au deposit was obtained for samples polarized between \(V_{eq}\) and \(-1.0\) V (Ag/AgCl). Furthermore, the transients are characterized by an initial increase of the current density which is followed by a decay at longer times. The time corresponding to the current maximum decreases and the maximum current increases as the applied potential becomes more negative. These results are consistent with nucleation of 3D hemispherical clusters followed by diffusion-limited growth.

**Figure 2.** Dependence of the C line height (a) and width (b) on the electron dose taken from AFM profiles of two arrays of ten E-beam C lines deposited on n-type Si\(\langle100\rangle\) using a beam energy of 5 (c) and 20 keV (d).

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\[ \text{AFM Height (nm)} \]

\[ \text{AFM Width (nm)} \]

\[ \text{Exposure Dose (C/cm²)} \]

\[ \text{Exposure Dose (C/cm²)} \]

\[ \text{Distance (µm)} \]

\[ \text{Height (nm)} \]
observed for several systems\textsuperscript{42-47} and can be attributed to the relatively weak interaction energy between semiconductors and metals. The morphology of the gold deposits obtained after current transient experiments have been studied by SEM (not shown). It has been observed that the density of nuclei as well as the size of the globular features depend strongly on the applied potential, \textit{i.e.}, the higher the cathodic applied potential, the larger the number of small crystallites. At a relatively low cathodic potential (\(-1.1 \text{ V vs. Ag/AgCl}\)) only a few crystallites with a typical feature size of 220 nm are deposited onto Si. Using a higher cathodic potential (\(-1.6 \text{ V vs. Ag/AgCl}\)) results in deposits entirely covering the Si surface with particles of a mean size of approximately 20 nm.

\textit{Resolution of the process.---}As the lateral resolution of the process at the edge of the C deposit depends strongly on the formation of a smooth and continuous film, the creation of a large number of small crystallites is required because the coalescence of islands in an earlier growth stage leads to homogeneous layers. Therefore, deposits are preferentially formed at high cathodic potential.

Figures 6a and b show an Si sample carrying the two series of C patterns as described above after electrochemical deposition of Au. Electrochemical treatment consisted of a potential step to \(-1.6 \text{ V (Ag/AgCl)}\) for 10 s. In accordance with our previous work, an E-beam C deposit in the nanometer range in thickness is sufficient to block the electrodeposition of Au and achieve a complete masking effect.\textsuperscript{30} From Fig. 6a, where C lines were deposited with a beam energy of 5 keV, it is apparent that independently of the electron dose the Au deposit between the C lines is homogeneous and smooth leading to an excellent lateral resolution. In contrast, if the C lines are written with a beam energy of 20 keV, the Au deposit becomes coarse between the patterns and the density of crystallites decreases when the electron dose increases. This so-called proximity effect\textsuperscript{48} observed for high electron doses is attributed to the backscattered electron (BSE) induced C deposition partially blocking the electrodeposition of gold in the immediate vicinity of the predefined patterns. It is reported that the contribution of BSEs for conventional resists can cause pattern distortions and limit the ability to resolve critical dimensions, but it can be reduced using high beam energies much greater than 20 keV\textsuperscript{49} or membrane substrates.\textsuperscript{50} According to the literature, the size of the interaction volume between electrons and the specimen is a function of the incident beam energy.\textsuperscript{51} As the beam energy is increased, the electrons can penetrate more deeply in the specimen and a more significant fraction of the incident electrons striking the surface re-emerge from the sample. Lateral scattering of the primary electrons as they penetrate the specimen gives rise to the narrowing of the distributions, the forward-scattering distribution. Backward scattering of electron from the substrate gives rise to the broader distribution, the backscattering distribution. The
spatial distributions of forward scattered electrons (FSEs) and BSEs are generally assumed to be Gaussian and depend strongly on the E-beam energy, i.e., the higher the accelerating voltage, the narrower the FSEs distribution and the broader the BSEs distribution. The disk from which electrons are backscattered from the substrate can be established through the determination of the Kanaya-Okayama range. At low beam energy (~5 keV), the BSEs distribution becomes narrower, as broad in space as the forward scattered component (Fig. 7a) so that the region to which the BSEs can escape is limited to a disk of approximately 0.47 μm in diameter. Thus, independent of the electron dose used, confined C lines with well-defined borders are deposited as depicted in Fig. 7b. As the energy of the incident electrons is greater (~20 keV), the interaction volume increases dramatically (approximately 4.7 μm). Thus, the circular region where BSEs re-emerge is significantly larger than the area exposed by the incident beam and FSEs (Fig. 7a). As a consequence, the region where adsorbed hydrocarbons decompose is considerably larger than the defined pattern locations. Since the contribution of the BSEs overexpose a large area, a diffuse C fog builds up in the vicinity of the beam impact and can hinder subsequent electrodeposition of Au. The amount of this additional C deposit increases with increasing electron dose and with reducing spacing between patterns because C fog overlapping occurs as depicted in Fig. 7b. From these results, it is clearly apparent that BSEs play a crucial role. At low-beam energy, the resolution of the process is mainly governed by the BSEs exposure and independent of the electron dose used, the resolution obtained at the edges of the C lines is excellent. At high beam energy, BSEs overexpose a large area and a relatively low electron dose is required to decrease the contribution of BSEs and achieve good lateral resolution.

In order to explore the lower size limit of the process, a Si sample carrying two perpendicular arrays of C lines with decreasing spacing were written with a 1 C/cm² electron dose using a 5 keV beam energy. In this case, a low beam energy was chosen in order to dismiss a possible C fog overlapping by reducing the spacing between patterns. Subsequently, electrodeposition of Au was performed by a potentiostatic experiment (~1.6 V [Ag/AgCl] for 10 s). Figure 8 shows that the features reveal a coherent formation of clusters completely separated by the C lines. The size of the dots decreases by decreasing the distance between the C lines and deposition of clusters in the sub-50 nm range can be achieved.

**Conclusions**

Under optimized electrochemical conditions, it has been shown that the E-beam energy used for depositing C-masks plays a crucial role. C patterns written with a relatively high beam energy (~20 keV) revealed the presence of a C background in the vicinity of the predefined patterns. The amount of this additional C increases with increasing electron dose. It is assumed that the large disk from which BSEs re-emerge from the sample have enough energy to decompose organic molecules adsorbed at the Si surface. As a consequence, such C fog surrounding the patterns can partially block electrodeposition of Au. Thus, poor resolution is obtained at the edges of the C lines not only for high electron dose but also when the background overlapping occurs by reducing the spacing between the patterns. Decreasing the spatial distribution of the BSEs by decreasing the beam energy can dismiss this overexposure. As BSEs mainly govern the patterning independent of the electron dose, the resolution of the process is considerably improved. In this case, Au clusters in the sub-50 nm range were successfully fabricated.
Figure 7. Schematic representation of the spatial distributions of the forward scattered electrons (FSEs) and the back scattered electrons (BSEs) for a beam energy of 5 and 20 keV (a) and the corresponding spatial distribution of C (b).

Figure 8. SEM image of Au dots fabricated by the E-beam induced C masking technique. A Si sample carrying two perpendicular arrays of C lines with decreasing spacing, written with a 1 uC/cm² electron dose using a 5 keV beam energy was electrochemically treated by a potentiostatic experiment [-1.6 V (Ag/AgCl) for 10 s]. The size of the Au nanostructures decreases by decreasing the distance between the C lines. Au dots in the sub-50 nm range in size can be fabricated.

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