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Macroporous silicon membranes as electron and x-ray transmissive windows

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Macroporous silicon membranes are fabricated whose pores are terminated with 60 nm thin silicon dioxide shells. The transmission of electrons with energies of 5 kV–25 kV through these membranes was investigated reaching a maximum of 22% for 25 kV. Furthermore, the transmission of electromagnetic radiation ranging from the far-infrared to the x-ray region was determined. The results suggest the application of the membrane as window material for electron optics and energy dispersive x-ray detectors. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1772519]

With the development of the environmental scanning electron microscope (ESEM), now the imaging of biological specimens under ambient conditions has become convenient. ESEMs enable the introduction of a wide variety of analytical techniques including energy dispersive x-ray spectroscopy (EDX) and cathodoluminescence into life sciences. The key requirement of the ESEM is the separation of the electron column, where the electron beam is formed and which has to stay under a high vacuum, from the sample chamber which can stay under ambient conditions. Conventionally, such a pressure gradient is formed by a cascade of differential pressure stages which are only connected by small apertures for the transmission of the electron beam. If an electron transmissive membrane could be introduced to separate the high vacuum electron column from the sample chamber directly, the setup could be much simpler and smaller. On the other hand a x-ray transmissive window is generally necessary to protect the cooled EDX detectors from contamination. This window often consists either of beryllium or a very thin polymer foil. With a strong beryllium window only characteristic x-rays with energies above 1 keV can be effectively detected. With the polymer foil this range can be extended down to 100 eV. However, polymer windows are very fragile. Here, we report on a kind of window material which consists of an array of holes in a silicon wafer supporting an ultrathin silicon dioxide film. The silicon provides the mechanical strength to withstand an atmospheric pressure drop, whereas the silicon dioxide films provide excellent electron and x-ray transparency.

We start the fabrication of the macroporous silicon membrane by the photolithographic definition of a two-dimensional (2D) hexagonal pattern of KOH etch pits on a (100)-oriented *n*-type silicon wafer.[1,2] These etch pits act as nucleation sites for the macropores which are subsequently etched photoelectrochemically in 5% hydrofluoric acid (HF) at a temperature of 10 °C applying a voltage of 2.8 V between the platinum cathode and the *n*-type silicon wafer. As electronic holes have to be supplied for the etch process, the *n*-type silicon wafer is illuminated from the back side with visible light. The pore diameter can thus be controlled via the illumination intensity. The resulting pores have a length of 50 μm and an average diameter of 2.46 μm. This corresponds to an average porosity of 31% of the transparent region (Fig. 1). The pores grow perpendicular to the surface along the [100] direction. After etching, the pore walls are covered with a layer of microporous silicon.

To remove the microporous layer and smoothen the pore walls the whole structure is oxidized for 3 h at 900 °C and the silicon dioxide layer subsequently etched away in HF. Afterwards the final thermal oxidation at 900 °C for 3 h leaves a 60 nm thick SiO_2 layer on the pore walls. Finally, the bulk silicon back side of the sample is removed in 25% KOH at 90 °C and 25% TMAH at 80 °C. When the etch process is stopped at the right time, the oxidized pore heads remain (Fig. 2). The resulting sample structure is a 50 μm thick macroporous silicon membrane whose pores are closed on one end with the dome-shaped SiO_2 shells of the former pore tips.

To determine the transmission of electrons through the SiO_2 shells, the sample is placed on top of a Faraday cup in a scanning electron microscope and is grounded. The electron beam is focused onto a single dome and an area of 240 nm × 360 nm is scanned. After penetrating the SiO_2 shell (Fig. 3 inset) the electrons travel through the 50 μm

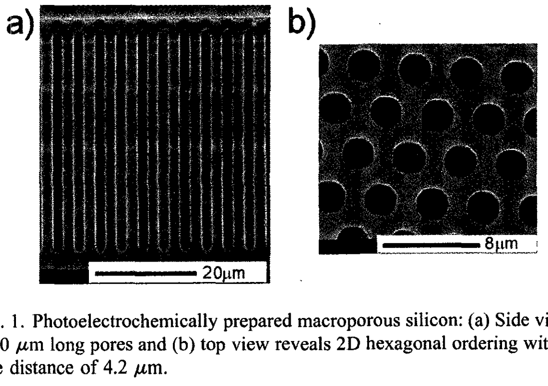

FIG. 1. Photoelectrochemically prepared macroporous silicon: (a) Side view of 50 μm long pores and (b) top view reveals 2D hexagonal ordering with a pore distance of 4.2 μm.

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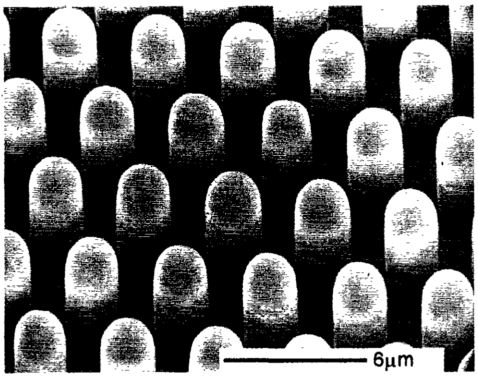

FIG. 2. Silicon dioxide shells formed after oxidation of pore walls and removal of bottom bulk silicon substrate.

long pore channel and after another 1 cm flight in vacuum enter the Faraday cup. For a reference measurement, the sample can be moved out of the electron beam so that the beam enters the Faraday cup directly. The ratio of measured current with and without the sample then defines the transmission of the membrane structure. This measurement is very similar to the one earlier reported by Doll *et al.*[3] which was used to measure the transmission through nanopores in alumina. In our case the energy of the electrons varied between 5 kV and 25 kV (Fig. 3). To obtain an average transmission for the ensemble of pores, the measurement was carried out for ten single pores. Although the values for the transmission vary from pore to pore, a clear increase of transmission with increasing electron energy (acceleration voltage) is observed. For the maximum applied acceleration voltage of 25 kV, the average transmission reaches 22%.

When the electrons enter the 60 nm oxide membrane, they experience elastic (Rutherford) and inelastic interaction with the silicon and oxygen atoms. As the mean-free-path length for elastic scattering amounts only to several nanometers for the considered electron energies, multiple scattering occurs. To simulate this, the Monte Carlo program "MC-Set" developed by Napchan[4] and based on the algorithm of Joy was used. The overall transmission for electrons in the range of 5 kV–25 kV through a 60 nm silicon dioxide membrane is predicted to range from 93% to 99.8%, values that are much larger than those observed experimentally. However, due to the multiple scattering of the electrons, their angular distribution upon exiting the membrane is widened. As the electrons still have to pass the 50 μm long pores, only a small fraction of electrons exiting the SiO_2 shell in a cone with 1.4° opening angle reaches the underlying Faraday cup directly. The rest hits the pore walls. From the Monte Carlo data, the exit angles were calculated and the fraction of these directly transmitted electrons was determined (dashed line in Fig. 3). It lies well below the experimental data. The reason is probably that not only the directly transmitted electrons contribute to the measured signal but also the electrons that bounce against a pore wall and are backscattered into the pore again.

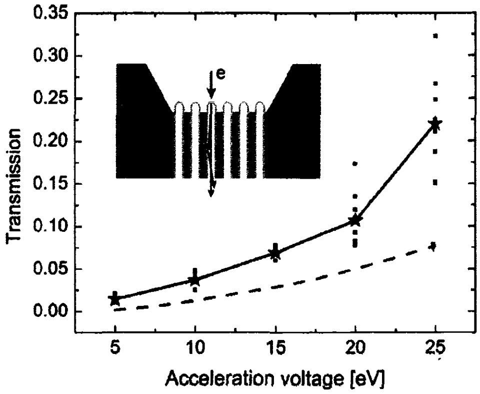

FIG. 3. Electron transmission through single pores with 60 nm oxide membrane on top. Squares show the transmission for every one of the ten measured pores while stars represent the average transmission at the corresponding energy. The solid line is a guide for the eye for the experimental values. The dashed line represents the calculated transmission of electrons through 60 nm of oxide into a cone with opening an angle of 1.4°. Inset: Measurement geometry.

For applications, as an electron transmissive membrane the 50 μm long pores are not ideal, limiting the amount of directly transmitted electrons. A reduction in length to the absolute minimum which is still necessary for stability of the structure is therefore desirable. On the other hand, turning the membrane by 180° may be advantageous. Then, the focused electron beam passes first through the pores and hits the oxide membrane at the end. In this way, the electrons exiting the whole structure experience only scattering inside the oxide membrane. The fraction of the electrons emitted with divergence angles below 5° is 45% of the incident beam at 25 kV and the sample would have to be brought within a distance of 100 nm to the membrane to achieve reasonable resolution. To decrease this divergence, the thickness of the membrane has to be reduced significantly. Alternatively, the objective lens of the ESEM should be placed after the membrane to refocus the divergent beam.

In addition to the ability to transmit electrons, the macroporous silicon membranes can also transmit electromagnetic radiation. To investigate this, the transmission spectra from the far infrared up to the soft x-ray region were investigated. For the infrared spectra, a Fourier transform infrared spectrometer was used. The spectrum in the far infrared was obtained using a KBr beamsplitter, a DTGS-Detektor, and a globar as lightsource. For the middle- and near-infrared measurements a CaF_2 beamsplitter together with a MCT-Detector and a tungsten lamp were used. For wavelengths above 10 μm, the macroporous membrane acts as an effective medium for the electromagnetic radiation as the wavelength is larger than the pore size and pore distance. The spectrum shows three major dips at 1080 cm^{-1}, 805 cm^{-1}, and 465 cm^{-1} which correspond to the absorption of the silicon dioxide films and are characteristic for the Si–O bond. For shorter wavelengths down to 1.2 μm, the transmission decreases. Possibly, the diffraction due to the 2D periodic pore lattice causes a transfer of energy from the zeroth-diffraction order to beams of higher diffraction order. As the limited acceptance angle of the instrument collects only the zeroth order, the light in higher orders is lost for the measurement. From 1.2 μm wavelength on a strong drop in transmission is observed. Around 800 nm, the transmission is quasi 0. It starts to rise again for wavelengths shorter than 500 nm (see inset of Fig. 4). This effect was previously observed by Lehmann[5] and can be explained qualitatively by considering the diffraction at the pore opening and the absorption at the silicon pore walls.

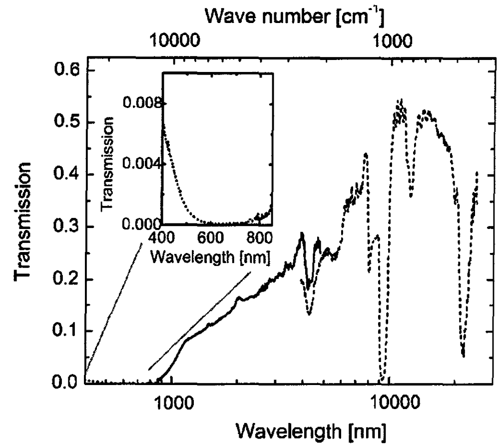

FIG. 4. Transmission from far infrared to visible. In the far infrared, pronounced absorption lines due to vibrations in the silicon dioxide membrane are observed. The transmission in the visible is quasi-zero as major parts of the light are diffracted at the entrance of the pores toward the absorbing pore walls. Inset: Increase of transmission for very short wavelengths due to reduced diffraction.

Finally, the transmission of the membrane in the soft x-ray regime was investigated employing the monochromized radiation of the plane grating monochromator beamline for undulator radiation at the electron storage ring BESSY II, Berlin, Germany. The transmission for the x-rays increases with increasing energy (Fig. 5). The marked positions in the figure show the absorption edges of the silicon K and L shells as well as for the oxygen K shell. As the wavelength in the energy region from 100–2000 eV is shorter than 13 nm, the pore dimensions are much larger than the wavelength, and diffraction no longer plays a significant role. The transmission can be discussed in terms of geometrical optics. The beam spot at the sample was approximately 350 μm $\times$ 350 μm so that a large number of pores was irradiated. For the soft x-ray regime, the absorption of the 50 μm long silicon pore walls is large so that the detected transmission occurs only through the SiO_2 shells. The maximum possible transmission is therefore limited to 31%, the value of the porosity, and is approached at higher energies due to negligible absorption in the SiO_2 shells.

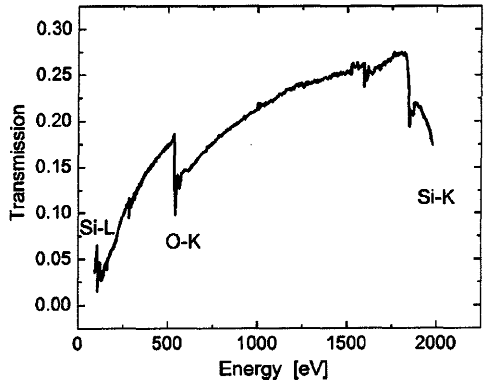

FIG. 5. Transmission for x-rays. The transmission increases for higher energies and approaches the limit of 31%. The absorption edges of silicon and oxygen atoms of the silicon oxide membrane are indicated.

The stability of the structure against pressure differences was measured by connecting one side of it to a vacuum chamber while the other side was exposed to the ambient atmospheric pressure. A pressure of 5×10^{-6} mbar was sustained in the chamber proving that the structure can withstand large pressure differences.

To increase the overall transmission for electrons or electromagnetic radiation both, the length of the macropores and the thickness of the SiO_2 shells, have to be reduced while the pore diameter (porosity) should be increased. This, however, makes the structure more fragile and an assessment of the strength of the structure is necessary. Two different parts of the whole structure determine its pressure resistance—the individual oxide shells and the area and thickness of the whole macroporous membrane. The dome-shaped oxide shells are approximated by hemispherical shells. A pressure p applied from one side of the shell causes a lateral stress σ_{membrane} at the cross section of the shell.

$$\sigma_{\text{membrane}} = \frac{pR}{2d}. \tag{1}$$

Here, R is the radius of the hemisphere and d the thickness of the shell. If the pressure is applied from inside the hemisphere, σ_{membrane} must not exceed the tensile strength of silicon dioxide of 48 MPa.[6] If we keep the pore lattice constant of 4.2 μm and assume a maximum realizable pore diameter of $R=2$ μm (porosity 82%) a minimum thickness of $d=2.1$ nm is required so that the shells still withstand atmospheric pressure. However, if the pressure is applied from outside the hemisphere, the dome is under compression. Now, the compression strength of SiO_2 (1100 MPa) sets the limit and a minimum thickness of $d=0.093$ nm is obtained. Although this value is unrealistic as it is close to one monolayer, it shows that a further reduction of oxide thickness is possible. A shell thickness of $d=10$ nm appears experimentally possible. If the pressure is applied to one side of the membrane, also a shear stress at the rim of the membrane where it is held by the bulk substrate, is caused. If we assume a square membrane with a side length of 2 mm and take the shear strength of silicon as $\sigma_{\text{shear}}=10$ MPa (Ref. 7) the thickness l of the membrane has to be at least $l=(pA)/(\sigma_{\text{shear}}u) = 5.1$ μm where p is the atmospheric pressure and A and u are the area of the membrane and its circumference.

In conclusion, we showed that a microscopic array of very thin silicon dioxide windows can be constructed on a macroporous silicon backbone. The silicon dioxide windows are transmissive for electrons, x-rays, and for near- to mid-infrared radiation. The whole membranes can withstand large atmospheric pressure differences so that they represent promising window materials for both ESEMs and EDX detectors.

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