CONTROLLED FORMATION OF THICK ANODIC FILMS OF MESOPOROUS SILICA

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Introduction

In dilute fluoride medium, p-Si voltammograms exhibit a fast-rising region, associated with formation of a porous silicon layer, followed by two electropolishing plateaus. An interfacial oxide film is then present and thickens with increasing potential. In a potential range ~3-8 V, the interface exhibits a resonant behavior, due to an oscillation of the film thickness on the local scale, whose origin is still controversial. The interfacial oxide film becomes porous above a critical potential on the order of 10 V [1]. Evidence for this porosity originates from the very different values of the film thickness as deduced from infrared spectroscopy and high-frequency capacitance measurements. Even more direct evidence for mesopore formation is provided by scanning electron microscopy. However, these porous films are very thin, because they are obtained in a dynamic regime, the fluoride electrolyte dissolving the film at the same time as it is formed. Here we report on the formation of mesoporous SiO_2 films as thick as several micrometers.

Principle and experimental

Instead of the acidic electrolyte used in our previous experiments, we have chosen a weakly alkaline fluoride electrolyte with a low buffer strength. The underlying idea is schematically shown in Fig.1. For a given fluoride concentration, the dissolution rate of silica decreases steeply when the pH value increases above 3-4. Typically, in a 0.1-1M fluoride medium of pH 8, the dissolution rate of SiO_2 is extremely low. However, if a porous SiO_2 layer starts forming, the current at the bottom of the pores may lead to a local pH decrease; hence, the local dissolution rate becomes high and pore growth may proceed. The porous layer is essentially preserved because pH in the body of the film reincreases due to the outdiffusion of H_3O^+ ions to the electrolyte.

p-type single-crystal silicon platelets were back contacted with a gold-aluminum ohmic contact and encapsulated with sticky wax in a PTFE casing. They were anodized in (0.7M NH_4Cl + 0.3M NH_4F adjusted to pH=8 by addition of minute amounts of NaOH) using a three-electrode cell. Voltammograms were recorded and constant-potential anodizations were carried out under mild stirring conditions. After anodization, the electrode was quickly removed from the electrolyte, rinsed in bidistilled water, dismounted and examined by SEM.

Results

Fig.2 shows a typical voltammogram. On the positive-going potential scan, the current is very low, till it increases steeply around 15 V. If the potential sweep is interrupted or even reversed at this stage, the current keeps increasing, and reaches a steady-state value, here on the order of a few mA/cm^2. This behavior can be attributed to the onset of formation of a porous layer. The high value of the current is more or less preserved on the negative-going potential scan, down to about 6 V where the current drops abruptly. This behavior, and especially the hysteretic behavior in the 6-15 V region, does not depend on the scan rate significantly.

Fig.3 shows SEM photographs of a porous layer formed at 12 V potential, after 5 min anodization in a (0.1M fluoride, pH 8) electrolyte. The oxide layer is 2 μm thick. The whitish flakes at its surface can be identified to precipitated silica formed by hydrolysis of fluorosilicate ions. The top view of the surface indicates the presence of a porous structure with characteristic sizes on the order of 10-15 nm. Notice that this figure is significantly smaller than that previously reported for films formed at potentials higher than 30 V [1].

Conclusion

Anodization of p-Si in unbuffered weakly alkaline fluoride electrolytes leads to controlled formation of mesoporous silica films. Formation of ordered structures of such mesopores does not appear presently beyond reach.

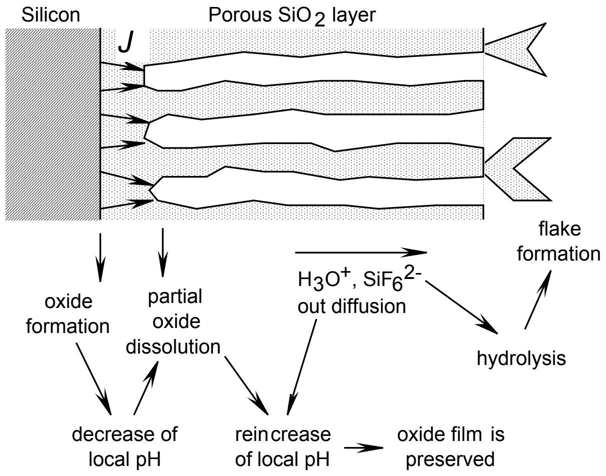

Fig. 1: Scheme of the mechanism of porous SiO_2 formation.

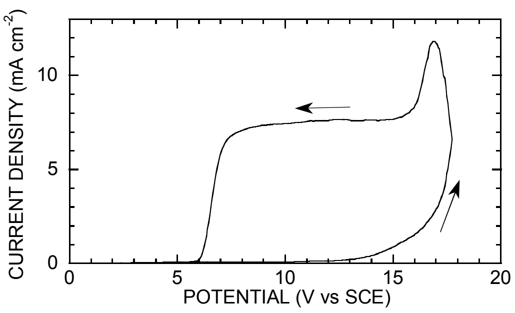

Fig.2: Voltammogram of p-Si in (0.3M fluoride, pH=8) electrolyte. Mild stirring. Scan rate 150 mV/s.

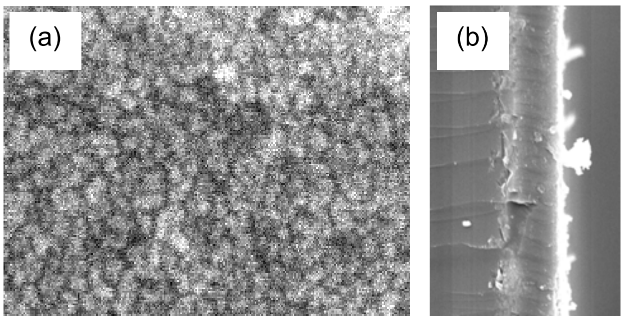

Fig.3: Top view (a) and side view (b) of a thick film of mesoporous silica.

References

[1] M. Lharch, J.-N. Chazalviel, F. Ozanam, M. Aggour, R.B. Wehrspohn, *Porous Semiconductors Science and Technology 2002* (Tenerife, march 2002), to be published in *Phys. Status Solidi (a).*