Porous silicon and Ni-nanostructures – a very versatile, but still poorly characterized material

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Introduction

Porous silicon (PS) can be obtained by anodization of a silicon substrate and in dependence on the doping of the wafer and the formation parameters a great variety of different structures can be created. PS exhibits specific properties ranging from light emission in the visible range to biodegradability and thus is a promising material for many future applications.

By a proper choice of the process parameters regularly arranged pores with a length of around 30 µm, a diameter of around 60 nm and thus an extremely high aspect ratio can be fabricated. The pores are oriented perpendicular to the surface. After the anodization, ferromagnetic metals like Nickel can be deposited within the pores by a galvanic deposition process.

To establish a relationship between the PS/metal – structure, its magnetic behaviour and the process parameters, definitely investigations by electron microscopy are necessary. However, both the preparation and investigation of porous materials poses a great challenge.

Structure of porous silicon

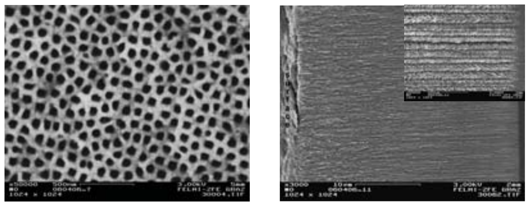

Fig. 1. SEM images of the surface (left) and the cross section (right) of an etched silicon wafer. The insert in the image right shows a part of the pores at higher magnification. The dendritic structure is due to the fact that etching in the (113) direction could not be completely suppressed. The pore legth is around 34 µm, the pore diameter around 60 nm.

Ni deposited within porous Si – structure and crystallinity

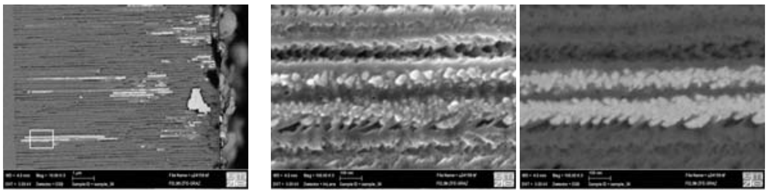

Fig. 2. left: Backscattered electron (BSE) image of a cross section (fracture surface) of porous silicon partialy filled with wire-like Ni – structures; centre: secondary electron (SE) image of the region marked in the figure left; right BSE image of the same area.

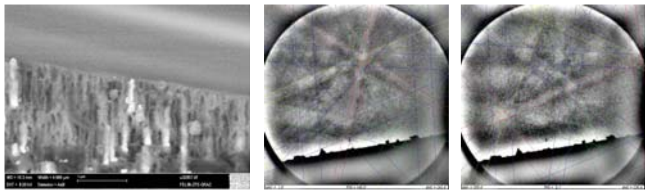

Fig. 3. left: BSE image of a cross section of porous silicon partily filled with wire-like Ni – structures; centre and right: Electron backscatter diffraction patterns from the points 5 and 6 marked in the image left (after image processing).

Ferromagnetic metals like Ni can be deposited within the pores by a galvanic deposition process. A complete filling of the pores is, due to their high aspect ratio and their dendritic structure, not possible. By variation of the deposition parameters both the shape of the particles (spherical, ellipsoidal, wire-like) and their distribution within the porous matrix can be controlled [1], and as a consequence also the magnetic properties of this PS/metal hybrid system can be determined [2, 3].

It is still not clear whether the wire-like structures are only individual particles in close contact to each other or real wires. In the SEM images parts of these "wires" are covered by the dendritic structures. The magnetic behaviour of these structures resembles that of wires. First investigations, performed by EBSD to avoid any preparation artefacts, seem to show that they are polycrystalline. But as the respective measurements are not made at flat surfaces, the calculated local orientations may be distorted.

TEM – investigations and preparation artefacts

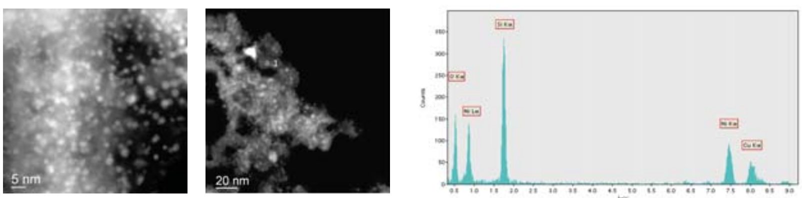

Fig. 4. Ni-filled porous silicon; left: STEM HAADF image of a FIB lamella; centre: STEM HAADF image of an ultra-microtomy section; right: EDX-spectrum from region 1.

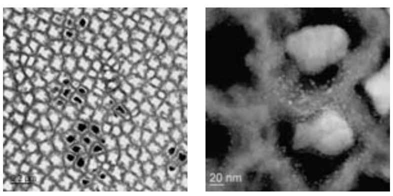

Fig. 5. BF and STEM HAADF images of Ni-filled porous silicon, from a FIB lamella cut perpendicular to the pores; the clustering of the particles can be observed.

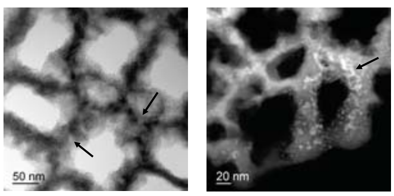

Fig. 6. Ni-filled porous silicon; FIB lamella cut perpen-dicular to the pores; left: BF image, zero loss filtered; right: STEM HAADF image.

The preparation of thin lamella of this porous system for TEM investigations poses a great problem. In case of FIB cuts both the porous material itself and the Ni-particles can be sputtered and redeposition of sputtered material can occur. Preparing thin sections by ultramicrotomy will cause a breakdown of the porous system.

Fig. 4 shows a comparison of HAADF images from both a FIB lamella and an ultramicrotome slice. In both images lots of small Ni-particles are visible. Thus they are not artefacts resulting from the FIB preparation. But it has not been proven yet, that the distribution of the particle sizes and shapes is the same for both specimens.

Fig. 5 demonstrates on one hand that clustering of particles occurs and on the other hand that the particles generally do not fill the whole pore diameter. However, also here sputtering effects could have an influence. The first impression is that the pore walls are dense, but Fig. 6 seems to prove the opposite: the existence of nano-sized channels between the pores (see arrows in Fig. 6 left). Nevertheless, the dendritic structure can make the interpretation of the contrast changes difficult.

Fig. 6 right definitely proves the presence of sputter and redeposition artefacts. Some of the cross sections of the pore walls, which should be pure silicon, are completely covered with Ni depositions (see arrow). Thus, as a conclusion, the development of new innovative, nondestructive and artefact free preparation methods is necessary in order to get reliable results.

References

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