Ionics liquids: an innovative medium for nanofabrication

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ABSTRACT

Porous silicon (PSi) is attracting a great attention as a breakthrough material with exceptional characteristics for microelectronics, layer transfer technology, solar and fuel cells, biomedicine, etc. Its properties can be modified by in introducing different materials into its pores. Ionic liquids (ILs) are known to be a smart medium to generate mono-disperse metallic NPs below 5 nm through a variety of processes (either chemical or physical). In this work, we demonstrate an efficient and safe "one pot" process to metallize PSi by decomposition of a metal-organic precursor in ILs.

1 INTRODUCTION

Porous silicon (PSi), discovered in 1956 by Uhlir,[1] is attracting a great attention as a breakthrough material with exceptional characteristics for microelectronics, integrated optoelectronics,[2] microelectromechanical systems (MEMS),[3] layer transfer technology, solar and fuel cells, biomedicine,..

The properties of PSi can be modulated by introducing different materials into its pores.[4] Indeed, the metallisation of Psi by copper can provide specific composite structures with new electrical, optical, magnetic, plasmonic, luminescent properties.[5-6-7]Copper incorporation can be carried out by electrochemical or electroless methods, by evaporation or sputtering deposition of Cu atoms,[6] and by supercritical fluid dry-process.[8] Quite recently, the formation of uniform film from copper metallic nanoparticles (CuNPs) has been reported.[9-11] The CuNPs, obtained from mesitylcopper (I) (CuMes) by H_2 reduction in the presence of octylamine as stabilizer, form a film when annealed. This film has a resistivity higher than the pure Cu, (10×10^{-6} Ω.cm vs. 1.72×10^{-6} Ω.cm for bulk Cu) due to the presence in the films of carbon inclusions resulting from organic materials used as NP stabilizer.

Ionic liquids (ILs) are known to be a smart medium to generate through a variety of processes (either chemical or physical) mono-disperse metallic NPs below 5 nm with well-defined morphology without any stabilizer.[12-13] Moreover, it has been shown that the resulting suspensions can be readily used with great success in several technological applications. Indeed, their relatively high thermal stability and low volatility are compatible with annealing conditions needed to achieve sintering of NPs and film formation.

The aim of this work is to develop an efficient and safe "one pot" process to metallize PSi by decomposition of a metal-organic precursor in ionic liquid. Recently we have reported that CuMes in ionic liquid is readily reduced under H_2 into a stable suspension of well dispersed CuNPs of 5 nm.[14] On the one hand, this suspension will be tentatively deposited onto PSi in an *ex situ* approach. On the other hand, the CuMes reduction will be performed *in situ* in the presence of PSi.

2 EXPERIMENTAL

All operations have been performed in the strict absence of oxygen and water under a purified argon atmosphere using glove box (MBraun) or vacuum-line techniques.

1-methylimidazole (> 99 %) 1-chlorobutane, was purchased from Sigma Aldrich and distilled prior to use. Distilled water, fresh distilled toluene (> 99 %, Sigma Aldrich) and fresh distilled dichloromethane (> 99 %, Sigma Aldrich) were used for purification of ILs bis(trifluoromethanesulphonyl)imide lithium salt (> 99 %, Solvionic) and mesitylcopper (CuMes) (Nanomeps) were kept in glove box and used as received. A solution of silver nitrate in distilled water was prepared in order to test traces of chloride in IL.

The synthesis of 1-butyl-3-methylimidazolium bis(trifluoromethylsulphonyl)imide, $[C_1C_4Im][NTf_2]$, was performed as reported in literature.[15] The purity was checked by NMR spectra, recorded on a Bruker advance spectrometer at 300 MHz for ^{1}H, at 75.43 MHz for [13]C. After purification, the halide content was found to be below 100 ppm (HR-SM), and water ~ 12 ppm, (limit of Karl Fischer titration).

2.1 Synthesis of copper nanoparticles

General procedure: in a glove box, CuMes was dissolved in $C_1C_4ImNTf_2$ in a Schlenk tube under stirring at room temperature to the desired concentration (5×10^{-2} mole.L^{-1}). 2 mL of this organometallic solution was canuled into an autoclave under argon. At this step, the reaction medium was warmed to the desired temperature without stirring. After gas purge, the autoclave was pressurized at 0.9 MPa of H_2 during 10 min. and kept at the selected temperature during 4h. At the end of the reaction, the resulting dark suspension was placed under vacuum to eliminate the

volatile by-products (mesitylene) and stored under argon in a glove box.

2.2 Surface sample and treatment

The porous silicon (PSi) material has been electrochemically generated in a hydrofluoric solution (HF) on a 200 mm diameter (100) silicon substrate with a high resistivity (1500 Ohm.cm). The 200 mm equipment is composed of a cleaning and an anodisation chambers and is fully automated. Anodic dissolution of silicon has been performed in a double tank cell where the silicon wafer was front and back sides immersed in the same electrolyte solution. This electrolyte was a hydrofluoric / isopropanol (IPA) mixture made of 5 volumes of HF (50 % weight) and 2 volumes of IPA. A 75 μm thick macroporous layer fully filled with microporous silicon has been obtained. Microporous silicon has then been etched partially after a 60 min immersion in a tetramethylammonium hydroxide (TMAH) solution at room temperature.

The experiments have been carried out on samples cut from the 200 mm wafer. As received, the surface of the samples exhibits a native oxide layer which appears when fresh silicon-wafer samples are exposed to air. The oxygen and humidity react with the silicon atoms affording ≡SiOSi≡ and ≡SiOH surface groups. Whenever required, the samples were deoxidized prior to metallization by immersion in a 1 % solution of hydrofluoric acid during 30 s, rinsed with deionized water and pre-dried with a nitrogen-air gun. Finally, all samples were kept under primary vacuum for one hour, then dried under high vacuum (10^{-5} bar, overnight), and stored in the glove box under argon.

2.3 Metallization of substrates

The metallization of the silicon samples has been realized through *in-situ* and *ex-situ* procedures.

In the *in-situ* experiments, the decomposition of CuMes was conducted in the presence of the silicon sample. In a glove box, a solution of CuMes in $C_1C_4ImNTf_2$ was poured on the substrate in an autoclave, then the reaction was carried out during 4h, at 100 °C, under 0.9 MPa H_2 and without stirring.

In the *ex-situ* modification, the CuNPs were first generated (4h, 100 °C, 0.9 MPa H_2 pressure and without stirring) in $C_1C_4ImNTf_2$. Then, in a glove box, on a PSi sample in an autoclave, this Cu-NP suspension with mean size of ~5 nm was added dropwise, and then the autoclave was kept under argon or H_2, 2h at 50 °C.

In both cases, after cooling down and depressurization of the autoclave, still in glove box, the sample was extracted from the reactional medium, washed twice with 2 ml of dichloromethane and dried under argon flow.

2.4 Characterization

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFT): The sample was dried by high vacuum (10^{-5} bar) overnight and transferred in a Harrick high temperature cell under argon into a Thermo Scientific Nicolet 6700 FT-IR equipment. The sample was initially purged for 20 min under 20 mL.min^{-1} of argon. An IR spectrum was recorded every minute between 25 and 350 °C (heating rate: 5 °C·min^{-1}) under 5 ml·min^{-1} flow of argon.

Belcat B: The temperature programmed desorption\ adsorption of wafers has been performed using a Belcat B device from BEL Japan to characterize the modification of silicon surface under annealing and to determine the H_2 quantity which is desorbed.

Specific surface measurement- BET: Nitrogen adsorption/desorption isotherms of samples have been obtained using a volumetric adsorption analyzer (ASAP2020) at −196 °C (77 K). Before the adsorption analysis, the samples were degassed overnight at 100 °C.

Transmission electron microscopy (TEM): The NPs were observed by TEM using a Philips CM120 at 120 kV. For this purpose, in a glove box, the suspensions of NPs generated *in situ* in IL were deposited on a TEM grid and transferred into the microscope without further preparation. For each suspension, the size of 200 NPs at least was measured. Their size distribution was then fitted by a lognormal law.

Scanning electron microscopy (SEM): an S-5000 high resolution scanning electron microscope from Hitachi was used to observe the morphology of the Si samples. For this analysis, 6x4 mm samples were cut and linked to an aluminum carrier with carbon colloids glue.

Electron dispersive X-Ray analyzer: another SEM, a Quanta 250 FEG FEI equipped with electron dispersive X-Ray analyzer (EDX) was used to probe the chemical composition of the samples.

3   RESULTS

Prior to metallization, both pristine and deoxidized macroporous silicon layers have been analyzed by DRIFT spectroscopy under argon atmosphere at 50 °C (Figure 1 left).
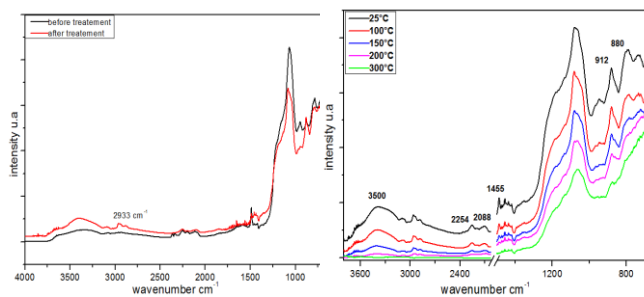

Figure 1: (left), DRIFT spectra of PSi under Ar at 50 °C, before and after HF deoxidation treatment. (Right) Temperature dependence of DRIFT spectra of deoxidized PSi under Ar, between 25 and 300 °C.

The main features of these spectra are an intense peak at 1100 cm^{-1} corresponding to the vibration of siloxane bridge (≡Si-O-Si≡), and broad pattern centered at 3500 cm^{-1} and at 880 cm^{-1} associated to the vibration of silanol groups

($\nu(\equiv Si\text{-}OH)$ and $\delta(\equiv Si\text{-}O\text{-}H)$, respectively). The intensity of these patterns depends on the chemical pretreatment of the substrate with HF solution. Note that in some samples, traces of carbohydrate groups (2933 cm-1 ν (CH) and 1455 cm^{-1} for δ ($\equiv Si\text{-}CH$) groups) have been observed; they are attributed to a pollution by grease during the pre-drying treatment with a nitrogen-air gun. Their intensity decreases with thermal treatment. The presence of very weak peaks at 2088 cm^{-1} and 2254 cm^{-1} is attributed to the vibrations of $\nu(\equiv SiH)$ and $\nu(>SiH_2)$ and the vibration at 912 cm^{-1} to $\nu(>SiH_2)$. The intensity of all vibrations assigned to the surface silane and siloxy groups decrease with temperature, Figure 1-right. This indicates that the SiH and SiH$_2$ groups are removed from the surface and pores upon annealing. Accordingly, the temperature programmed desorption performed on 0.108 g of PSi shows only one peak of H$_2$ desorption corresponding to 0.055 mmol.g^{-1}of H$_2$ at 500 °C confirming the presence of a small amount of surface silanes in the samples.

In a first experiment to metallize PSi, a well dispersed suspension of 5 nm CuNPs in C1C4ImNTf2 has been used following the *ex-situ* approach. Both HRTEM and XPS analyses indicate that this suspension only contains crystalline metallic zero-valent CuNPs.[14] The SEM images and EDX analysis of the metallized sample show the presence of Cu only on the surface but not within the pores, Figure 2. Consequently, the *ex-situ* procedure is not efficient to metallize the internal surface of the pores.
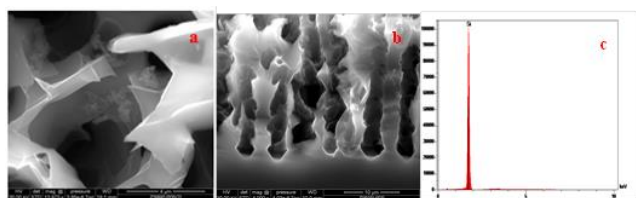
Figure 2: PSi sample tentatively metallized following the *ex situ* procedure. (a) Cu aggregates are visible on the surface, but (b) not in the pores as confirmed by (c) EDX measurement

On the contrary, after treatment through the in situ procedure, Cu islands are present at the surface as well as deep in the pores, Figure 3a. Indeed, EDX mapping (Figure 3b) shows that Cu is coating the inner walls of the macropores: only Si is visible on the cleaved cross section (orange), whereas Cu is detected within the hollow macropores (blue and green). The highest Cu concentration is detected at the pore walls near the cross-section plane (red). This uniform coating of the porous structure by Cu is further supported by a strong decrease of the specific surface of PSi from 89 to 57 m^2.g^{-1}.
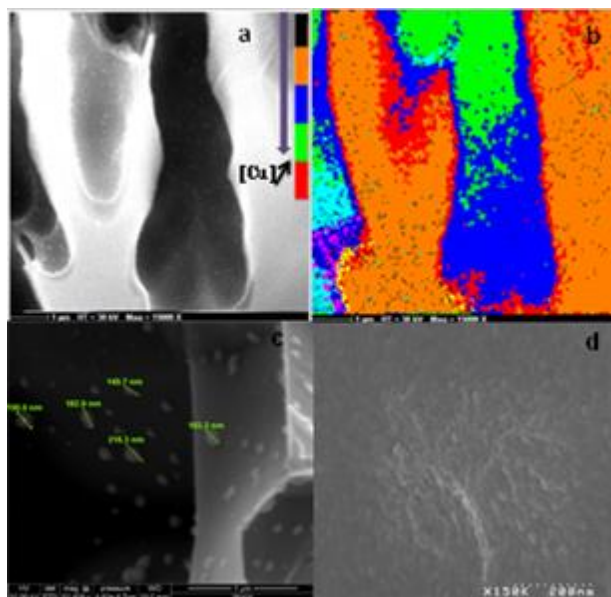
Figure 3: PSi sample tentatively metallized following the in situ procedure. (a) Cu islands are clearly visible in the poares, as confirmed by (b) EDX mapping of the ratio between Cu (red) and Si (orange). The size of these Cu islands is about (c) 200 nm on the flat walls of the macropores and (d) 12 nm on the microporous walls of the macropores.

A closer examination of the morphology of the Cu deposit shows that it is formed of large (>150 nm) Cu islands on the flat walls of the pores (Figure 3c) and smaller ones (about 12 nm) on the microporous walls of macropores (Figure 3d). This could be related to the difference in roughness (rougher surfaces induce more nucleation), or to the presence of surface groups (such as silanes) specifically in the micropores. Indeed, silicon surface groups such as $\equiv Si\text{-}OH$ and $\equiv Si\text{-}H$ could be involved into the NP formation and coalescence: the reaction of CuMes with surface $\equiv Si\text{-}OH$ of silica affords copper siloxy [$\equiv Si\text{-}OCu$],[16]. This copper siloxy could be reduced under H$_2$ generating a "seeded aggregative growth "of copper. This question is being investigated.

As a tentative to increase Cu content within the porous layer, temperature was increased. The *in-situ* deposition has thus been reproduced at 150°C and at 200°C under 0.9 MPa H$_2$, 4h. To estimate Cu content, low magnification SEM images have been recorded using a back-scattered electron detector (BSED), Figure 4. This analysis shows that upon increasing temperature to 150°C fosters Cu deposition within PSi: more Cu is detected throughout the porous material. This is expected, since higher temperatures facilitate both the penetration of the liquid in the pores and the decomposition of CuMes. However, when temperature reaches 200°C, the latter takes over: the decomposition reaction is too fast, and Cu is preferentially deposited near the surface, blocking access to the pores below.
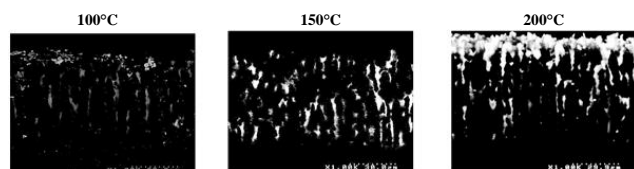
100°C   150°C   200°C

Figure 4: CuNP modified PSi wafer after treatment through in-situ procedure at different temperature(100°C, 150°C, 200°C) using back-scattered electron detector BSED.

4 CONCLUSION

In this work, the metallization of PSi has been investigated using an innovative, mild, and low-cost process using ionic liquids. In a first approach, the porous material has been impregnated by preformed suspensions of CuNPs in IL (*ex situ* procedure) with mitigated success, as almost no Cu was deposited inside the pores. Only the coalescence of the CuNPs into large islands was observed at the sample surface. Conversely, the impregnation by a solution of CuMes followed by the decomposition reaction (*in-situ* procedure) afforded uniform coating of the pores by Cu. Large Cu islands were formed of the flat walls of the macropores, whereas much smaller ones were observed on the microporous walls. It was found that by increasing the temperature, better penetration of the liquid and faster decomposition both contribute to increase Cu content in the pores. However, if the decomposition is too fast, Cu may aggregate on the surface, blocking access to the pores. To further understand the mechanisms at play during deposition, the precise role of the each surface group is currently under investigation in order to develop a versatile low cost and greener procedure.

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