COMMUNICATIONS

Blue photoluminescence from *in situ* Cu-doped porous silicon

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We have observed weak blue photoluminescence from *in situ* Cu-doped porous silicon formed by electrochemical etching with a low etching current density that is aided by cuprous chloride [Cu(I)Cl]. Fourier transform infrared spectroscopy, x-ray photoelectron spectroscopy, and Auger electron spectroscopy reveal that the blue emission is associated with formation of the carbonyl group that is catalyzed by Cu on the surface of the porous silicon. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1476961]

The observation of visible room-temperature photoluminescence (PL) from porous silicon (PS)[1] has stimulated many studies for potential applications in silicon-based optoelectronics. Metal deposition on PS is needed to realize potential applications in optoelectronics. There are many techniques available for the deposition such as vapor deposition, sputtering, electrodeposition, and immersion plating. Immersion or electroless plating refers to the plating of soluble metal ions onto a base material without applying a bias. Several authors have investigated the PL properties and chemical composition of metal-doped (Cu, Ag, and Au) PS,[2–9] in particular by the immersion plating method. Typical metal content is about 10 at.%. Often, the PL of PS is quenched by the deposition, and the oxidation of PS occurs simultaneously with the metal deposition.[2,3,6]

Recently, we reported ambient full-color PL from PS that was obtained through electrochemical etching aided by an ''oxidative'' metal such as Zn without any postanodizing treatment.[10] In the course of the etching, Zn deposition does not take place and therefore Zn plays a role in altering the luminescence characteristics. If we use a ''reductive'' metal such as Cu, which has a higher reductive potential than hydrogen, it is expected that PL quenching occurs during etching due to the deposition of Cu ion unto the surface.

Copper is known to promote chemisorption of carbon dioxide at room temperature with the aid of adsorbed oxygen to give a surface carbonate.[11] In addition, adsorbed carbon compounds such as alkanes could be more easily oxidized because of the ''reductive'' nature of copper. Once PS is formed and exposed to air, it undergoes aging with some regions attacked by carbon compounds. As PS has a large surface area, the formation of carbonyl group (C=O) could be facilitated under the catalytic action of copper. Huang[7] has given an experimental evidence for the formation of carbonyl group. He reported that two new peaks appeared at

1720.3 cm^{-1} and 2949.2 cm^{-1} from Fourier transform infrared spectroscopy (FTIR) measurements when the as-prepared PS sample was dipped into a dilute aqueous CuF_2 solution. Although the two new peaks were not discussed, it is clear that they originate from carbon contamination (C=O for 1720.3 cm^{-1} and CH_x for 2949.2 cm^{-1}). When carbon is incorporated into PS, PL properties do change and frequently blue PL is detected from carbonyl (C=O) compounds.[12,13]

In this communication, we report weak blue PL from *in situ* Cu-doped PS formed by electrochemical etching with a low etching current density that is aided by cuprous chloride [Cu(I)Cl].

Porous silicon samples were prepared with 1–10 Ω cm *p*-type (100) Si wafer by electrochemical etching at a constant current density of 5 mA/cm^2. Aluminum was sputtered onto the back side of the wafer for ohmic contact. We dissolved cuprous chloride [Cu(I)Cl] in a HF electrolyte solution (HF:CH$_3$OH:H$_2$O=2:3:5) to make a 0.01 molar solution of CuCl. The etching time was 5 min. After the anodization, the sample was rinsed in distilled water and dried by N$_2$ blowing. During the electrochemical etching, oxidation of Cu$^+$ does not occur since the ion is known to be stable in water environment.[14]

The PL spectrum of the sample was measured by the third harmonic of a Spectra-Physics *Q*-switched Nd:YAG laser (wavelength 355 nm) with a 360 nm filter. The pulse width produced by this laser is about 7 ns. The PL was detected by a Hamamatsu photomultiplier tube and the signals were then summed and averaged using a boxcar averager (Stanford Research Systems).

Ambient room-temperature PL measurement shows that no PL can be detected from the as-prepared sample. At the low current density and short etching time used in our experiment, the etching is negligible (porous layer ~200 nm) and the surface of PS is considerably covered with copper (about 53 at.% from Auger electron Spectroscopy measurement). However, a weak blue emission (wavelength =433 nm) was observed after aging for 1 day as shown in
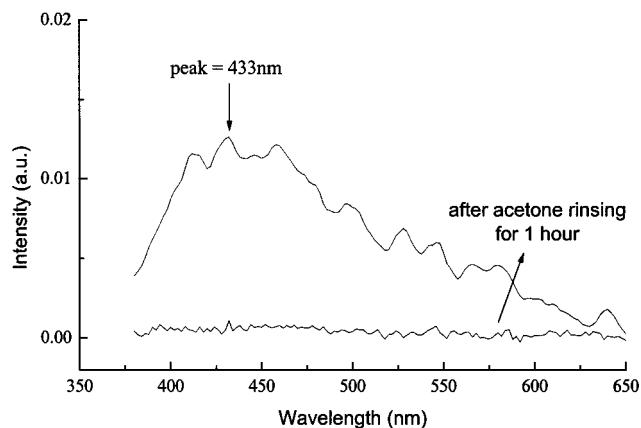
FIG. 1. PL spectra of the *in situ* copper-doped PS with etching current density of 5 mA/cm^2 after aging for 1 day. Note that no blue emission is observed after acetone rinsing for 1 h.

Fig. 1. This fact indicates that the blue emission may not originate from PS microstructure. After acetone rinsing for 1 h, no blue PL was detected, which shows that the blue emission is probably from carbon contamination. Several authors also presented the possibility that the carbon contamination, especially C=O bond, gives rise to blue emission.[12,13] However, identifying the exact structure and surface bonding that is relevant to the blue emission would require further study.

To elaborate on the mechanism of the blue emission at low current density, FTIR spectra (BOMEM, MB100 with a resolution of 4 cm^{-1}) were examined for the etched sample. The spectra are shown in Fig. 2 together with the spectrum for the conventional PS for comparison. For the sample prepared with the *in situ* copper doping, the peak intensity of the Si—O—Si stretching is relatively larger than that of the conventional PS, which is due to the following coupled redox reaction:[3]

Oxidation: $Si + 2H_2O \rightarrow SiO_2 + 4H^+ + 4e^-$
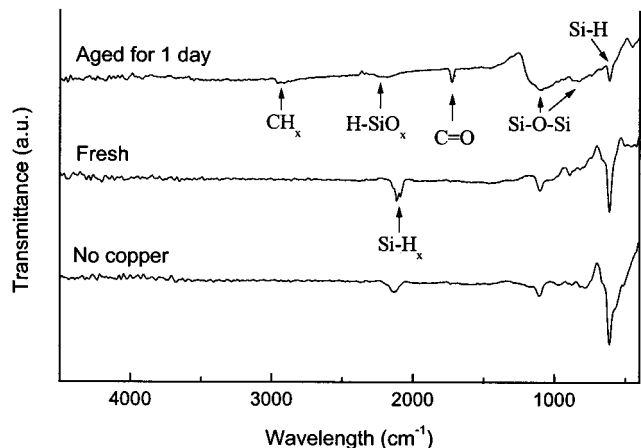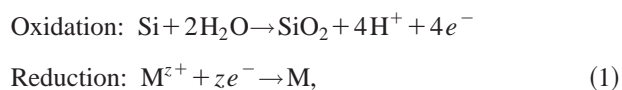
Reduction: $M^{z+} + ze^- \rightarrow M,$ (1)

FIG. 2. Transmittance FTIR spectra of the *in situ* copper-doped PS. The spectrum of the conventional PS at the same etching current density is also shown for comparison. Note that the C=O peak drastically increases after aging for 1 day.
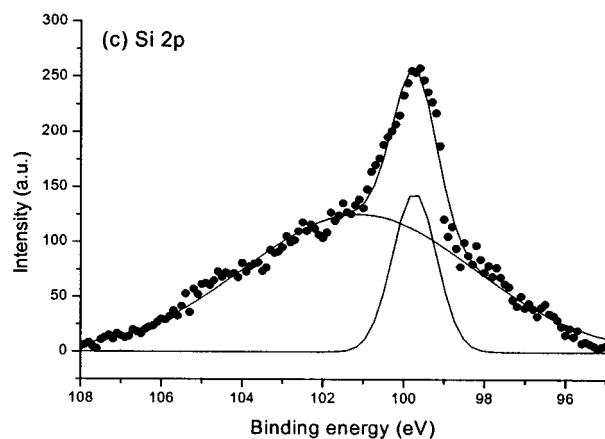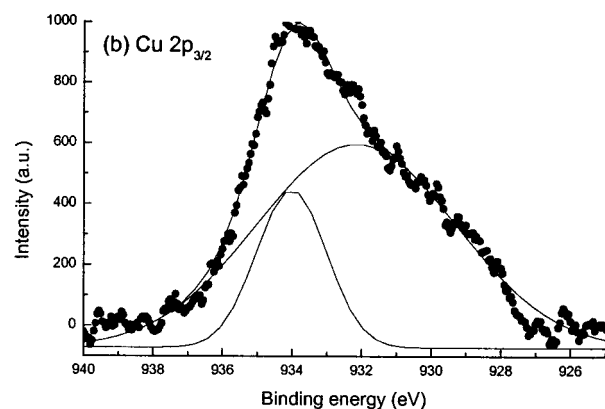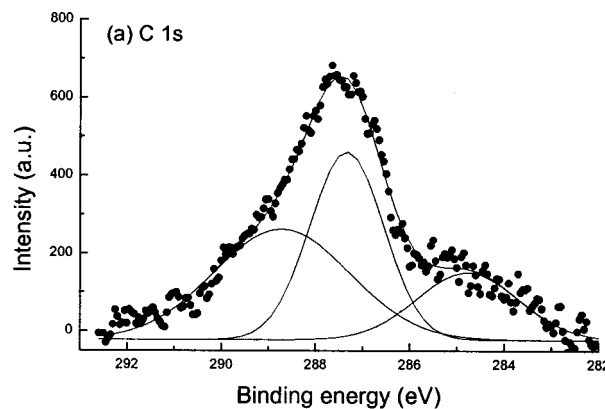
FIG. 3. XPS spectra of the aged *in situ* copper-doped PS. Spectra of (a) C 1s, (b) Cu 2$p_{3/2}$, and (c) Si 2p are shown with deconvoluted Gaussian peaks.

where M is the metal with z valence. This finding is consistent with the earlier reports that the oxidation of PS occurs simultaneously with metal deposition.[2,3,6] The Si–H$_x$ (2090–2150 cm^{-1}) stretching mode is known to be observed for the freshly etched sample and the H–SiO$_x$ stretching mode peaked around 2190–2250 cm^{-1} is typical of the aged sample. Other peaks are related to carbon contamination. In the copper-doped sample, we also found weak C=O bond and its peak intensity increases rapidly as the aging time increases as shown in Fig. 2.
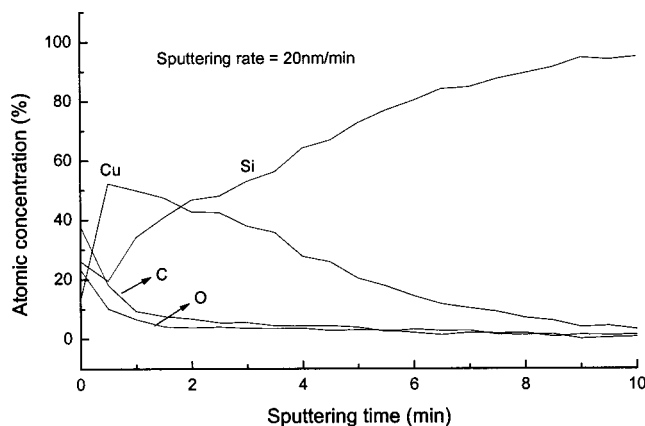
FIG. 4. Auger depth profile of the aged *in situ* copper-doped PS.

Similar results were observed in x-ray photoelectron spectroscopy (XPS) (SSI, 2803-S) for the PS sample aged for 1 day. The measurement was carried out at a base pressure of 10^{-9} Torr with a resolution of 0.48 eV. The XPS spectra were calibrated with carbon peak at 284.6 eV. Figure 3 shows the spectra for C $1s$, Cu $2p_{3/2}$, and Si $2p$ peaks. The C $1s$ spectrum for the sample consists of three peaks at 284.6, 287.3, and 288.7 eV. The peak at 284.6 eV is assigned to alkyl compound (CH_x) and the other peaks at 287.3 eV and 288.7 eV to carbonyl compounds (CO_x). It is noted that the carbonyl compounds are dominant species. Cu $2p_{3/2}$ spectrum shows two peaks at 932 eV and 934.2 eV. The peak at 932 eV is assigned to Cu or a small amount of Cu_2O. Although Cu_2O is a luminescent material,[15] its effect can be excluded since the blue emission disappears after acetone rinsing. The peak at 934.2 eV is assigned to CuO or $Cu(OH)_2$.[14] The Si $2p$ spectrum has two peaks at 99.5 eV and 101.2 eV, which are assigned to Si and SiO_x ($x<2$). Noting that the SiO_2 peak is known to appear at 103.4 eV,[2] the silicon oxide on the surface is rather silicon rich.

Figure 4 shows Auger (PHI Model 660) depth profile of the aged sample. The measurement was carried out at a base pressure of 5×10^{-9} Torr and the sputter depth was calibrated with SiO_2 etch rate. As shown in Fig. 4, copper concentration is 53 at. % at the surface and penetrates as deep as 200 nm. Similar depth profile has been reported for Ag immersion in Ag_2SO_4 solution.[4] Carbon concentration at the surface is about 38 at. % and exponentially decays into the depth. On the other hand, the carbon concentration at the surface for the conventional aged PS is at most 3 at. %.

The *in situ* Cu-doped PS has several features compared with the *ex situ* Cu-doped one. First of all, the atomic concentration of copper on the PS surface is considerably larger (~50%) than that of *ex situ* method (~10%), which provides a possible way of making good contact at PS–Cu interface. This is due to the fact that the copper deposition takes place simultaneously with the oxidation of PS. In the *in situ* Cu-doped PS, as-formed SiO_2 is etched by HF electrolyte, thus providing further sites for copper deposition. As a result, deposition and etching steps are repeated throughout the etching. On the other hand, the copper deposition is hindered by the hydrogen passivation on PS in the *ex situ* method, which results in a decrease in the amount of copper deposited.

Furthermore, the *in situ* method removes inevitable PL from the PS microstructure that would give red emission. If *in situ* Cu-doped PS could be used for carbon detection, the red PL would overshadow the blue emission for carbon detection. As PL is completely quenched by the doped copper during the electrochemical etching, the PS merely plays a role as a base material for large surface area, which acts as adsorption sites for carbon incorporation. Indeed, blue PL was observed for *in situ* Cu-doped PS only after aging 1 day as compared with as long as 35 days for the PS aged in plastic containers.[12] If one hopes to obtain red emission, it is sufficient to increase the etching current density and time, which is confirmed by our experiment.

In summary, we report blue emission from the *in situ* copper-doped PS mediated by carbon contamination. The relatively large Cu concentration at the surface would provide a possible way of making a good contact at the PS–Cu interface. The ability of PS to adsorb carbon rapidly could be used for detecting carbon compounds.

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