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# The optical properties of porous silicon produced by metal-assisted anodic etching

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**Abstract** Porous silicon (PS) was obtained from n-type (100) mono-crystalline silicon wafers with different metal using two different illumination conditions. The visible photoluminescence (PL) may come from defect-related radiative centers on PS surface and adsorbed hydrogen atoms may be associated to the elimination of irradiative centers on PS surface, which can be proved by the infrared absorption spectra. The metal can be used as catalytic role to increase the etching rate under back illumination, but under front illumination, the metal can cancel light-generated carrier leading to the decrease of etching rate during anodic etching. Furthermore, the change of minority carrier lifetime is opposite to the change of PL efficiency of PS, which can be Confirmed by the results of $\mu$-PCD measurements.

## Introduction

The observation of visible PL from PS at room temperature has stimulated extensive research for its potential application in silicon insulator, opto-electronic technology and optical interferometric biosensor etc [1, 2]. It was well known that optical properties of PS layer were strongly depended on type and resistivity of starting silicon substrates as well as on electrochemical parameters applied during the anodic etching process. It was reported that PS luminescence changed when metal element was introduced during or after electrochemically etching. Furthermore, the controlled deposition of metal on PS enhanced the activity of semiconductor electrodes for potential opto-electronic application. Many papers haves been published on PL in PS layers by post-chemical process. Shelomin et al. [3] reported that processing PS in HCl + Zn increases PL intensity by more than a factor of 2. A strong enhancement in the intensity of 0.98 μm emission of $Yb^{3+}$-ions in PS is obtained by adding a pre-annealing process to host PS in $O_2$ or $H_2$ prior to $Yb^{3+}$-ions incorporation and subsequent post-dope annealing [4]. Bondarenko et al. [5] researched the 77K PL and PL excitation spectroscopes of Er ions incorporated with Fe in oxidized PS in the form of 5–50 nm sizes clusters containing Fe, O and Er. High concentration of metals, such as Er, Cu and Zn, were electrodeposited onto PS. Er doping was found to improve the room-temperature visible PL of PS layer, whereas Cu and Zn doping seemed to have a quenching effect [6]. The effect of the presence of a metal ion on electrochemical etching process also has been extensive researched for recent years. Suh et al. [7, 8] researched that Zn used in anodic etching plays a role in altering the luminescent characteristics. Deliang Zhu [9] reported that the stable PL was achieved in iron-passivated PS. Furthermore, PS with strong and stable red PL prepared with chemical anodization of gold plated substrate was reported by Chen and Chen [10]. In addition, blue PL from in situ Cu-doped PS was reported in other published paper [11]. In other papers, PS has been made by chemical etching in $HNO_3$/HF solutions. A thin film of Au, Pt, or Au/Pt is deposited on the (100) oriented Si surface prior to immersion in a mixed solution of

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HF and $H_2O_2$. By controlling deposited metal type and doping type and doping level of Si, PS with different morphology and different light emitting property were produced [12, 13].

The bulk minority carrier recombination lifetime of semiconductor materials has become an important electrical parameter, which depended on the purity of semiconductor material and is significantly degraded by the presence of electrically active defect centers in bulk wafer: point defect (impurity centers or intrinsic defects) and crystal imperfections such as micro-defects or dislocations. The microwave-detected photoconductivity decay measurement ($\mu$-PCD measurement) is a non-contact and very quick technique, which always used to detect bulk minority carrier recombination lifetime.

This report described the influence of different metal element on PL, morphology and minority carrier lifetime of PS that were measured by $\mu$-PCD technique. The different illumination conditions during anodic etching also were proved to alter the effect of metal element on physical and optical properties of PS.

## Experiments

The PS samples were prepared using 1–10 Ωcm n-type Si (100) wafers by electrochemical etching at a constant current density of 30 mA/cm$^2$ for 10 min. Before etching, An aluminum film was sputtered onto back side of wafers for ohmic contact and the metal elements, such as Ni, Zn and Au, were sputtered on front side of silicon substrate, respectively, and then these silicon substrates are annealing in nitrogen at 400 °C for 30 min. Etching solution was composed of 48% hydrofluoric acid and ethanol in volume ratio of 1:2. Back or front illumination was supplied by white light from a 50 W halogen lamp. After anodic etching, PS were rinsed with de-ion water and dried in air.

The room temperature PL spectra of PS in the visible range were taken on a HITACHI F-4500 fluorescence spectrophotometer with a fixed excitation wavelength of 360nm. Scanning electron microscope images were obtained with a field emission FEI SIRION FESEM using an accelerating voltage of 5.0 kv. The infrared absorption spectra were taken using a Bruker IFS 66v/S FTIR spectroscope. $\mu$-PCD measurements were performed on the surface of PS using a WT-2000 lifetime scanner with a 904 nm wavelength light. All the measurements were carried out at room temperature.

## Results and discussions

Ambient room-temperature PL spectra of as-prepared samples with different metal aid under back illumination were shown in Fig. 1a. As shown in this figure, the intensity of PS luminescence increased monotonically as the assisted metal varied from Zn to Ni. In contrast, the wavelength of PS luminescence showed a quite different behavior and was stable with the variation of assisted metal.

In order to investigate the origin of PL spectra of PS with different metal aid, the FTIR spectra of corresponding samples also were shown simultaneous in Fig. 1b. The bending mode of $SiH_2$ is located at about 914 cm$^{-1}$ and the 2111 cm$^{-1}$ peak is related to the Si–H stretching mode. The peak at 1110 cm$^{-1}$ is from the O–Si–O stretch mode and the peak near 622 cm$^{-1}$ can originate from either Si–H wagging mode or Si–Si bulk vibration [14]. The change of intensity of Si–H stretching mode showed a same tendency with the variation of PS luminescent intensity, as shown in Fig. 1.

Many models have been proposed to explain the PL origin in published papers, which concluded pure quantum confinement model [15] or the defects on Si complexes surface [16–20]. In our experiment, Raman spectra of corresponding PS exhibited no quantum effect on PL emission, so the visible emission may produce by the recombination of light-generated carriers and surface defect states. The hydrogen atoms played a key role to

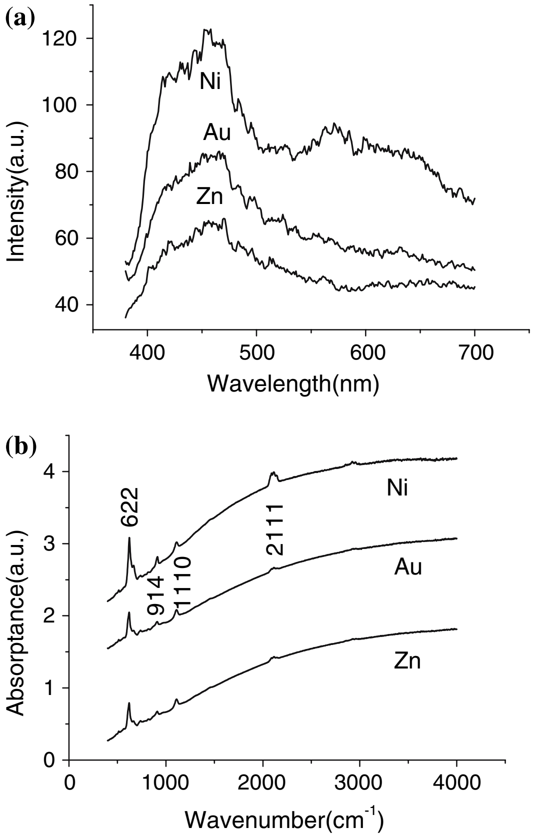

**Fig. 1** PL spectra (**a**) and FTIR spectra (**b**) of as prepared PS with different metal-aid under back illumination

eliminate irradiative centers on PS surface. This result can further be proved by $\mu$-PCD measurements.

The effect of metal on PL was investigated by SEM observation. The Fig. 2 gave surface morphologies of corresponding PS. The surface morphology of PS without metal aid also showed in Fig. 2a. The top view images of as prepared PS all showed columnar pores with a diameter in the range of several-hundred nanometers. In refs. 3, 7 and 8, the Zn-aid PS resulted in a more amorphous structure, higher strain in the film and a higher oxidation level, which may be associated with the increase of PL efficiency. In refs. 12 and 13, deposition of metal layer on Si wafer surface before chemical etching may result in different morphology and different light emitting properties, in which the metal film played as a catalytic role. In our experiments, the metal may also play as catalytic role to increase the electrochemical etching rate during electrochemical etching process, so the porosity and the pore density increased with metal element varied from Zn to Ni. Furthermore, as shown in Fig. 1a, the PL intensity increased with the increase of catalytic effects of metal element used in our experiments, which are same with the results in ref. 12 and 13.

Figure 3 showed minority carrier lifetime signal mapping and distribution of PS without or with Au aid. The different color on images represented different minority carrier lifetime in different region. The ring with yellow-color was played as the boundary between porous silicon and silicon crystal. Deep red-color region indicated porous silicon was existed in certain area with larger etched rate. By introducing an Au film into Si wafers surface before etching, PS porosity increased and minority carrier lifetime of PS decreased from 24 µs to 10 µs, as shown in Fig. 3. The minority carrier lifetime is dependent on crystal imperfections, such as micro-defects or dislocations. Due to the increase of PS porosity, the quantities of surface defects may increase simultaneously, which played as irradiative centers or radiative centers and lead to the decrease of minority carrier lifetime. In addition, minority carrier life of PS decreased with the increase of catalytic effects of metal element, which also proved our conclusion about the origin of PL emission that may be related to PS surface defect states.

Furthermore, residual metal on PS surface can effect minority carrier lifetime, which was proved by published papers [21, 22]. The minority carrier lifetime determining the efficiency of silicon solar cell is sensitively dependent on the concentration of metallic impurities, which formed electrically active levels in the band-gap and acted as minority carrier recombination sites to decrease minority carrier lifetime. In our experiment, deep color-ratio region contained remnant metal represented smaller minority carrier lifetime, as shown in Fig. 3b. In addition, the residual metal on PS surface also can supply in situ electrical contact sites to fabricate opto-electronic devices.

The PL spectra and the FTIR spectra of PS prepared with metal-aid under front illumination were shown in Fig. 4a and b, respectively. It was found that the change of Si–H vibration intensity is similar to that of PL intensity. The porosity and the pore density of PS were monotonic decreased with variation of metal element from Zn to Ni, as shown in Fig. 5. Preliminary results also showed that the

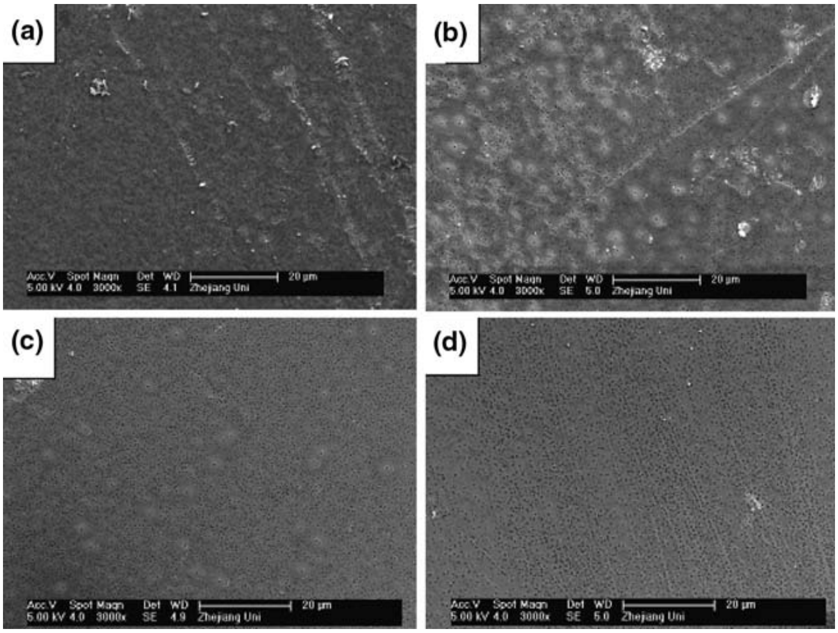

**Fig. 2** SEM images of as prepared PS without or with different metal-aid under back illumination. (**a**) no metal; (**b**) Zn, (**c**) Au; (**d**) Ni

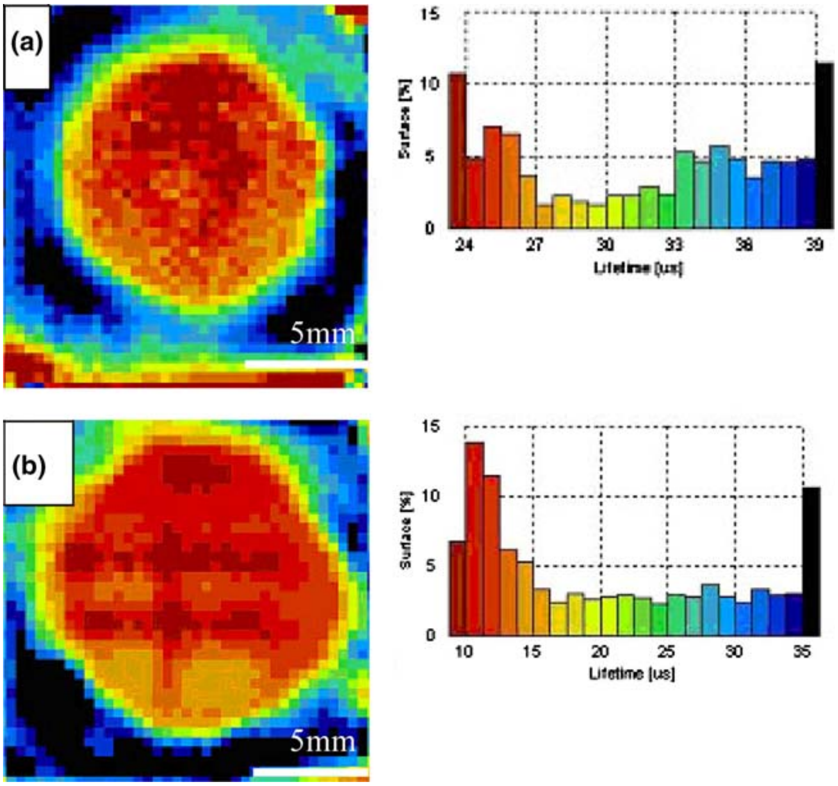

**Fig. 3** $\mu$-PCD images and minority carrier lifetime distribution of as prepared PS without (**a**) or with (**b**) Au-aid under back illumination

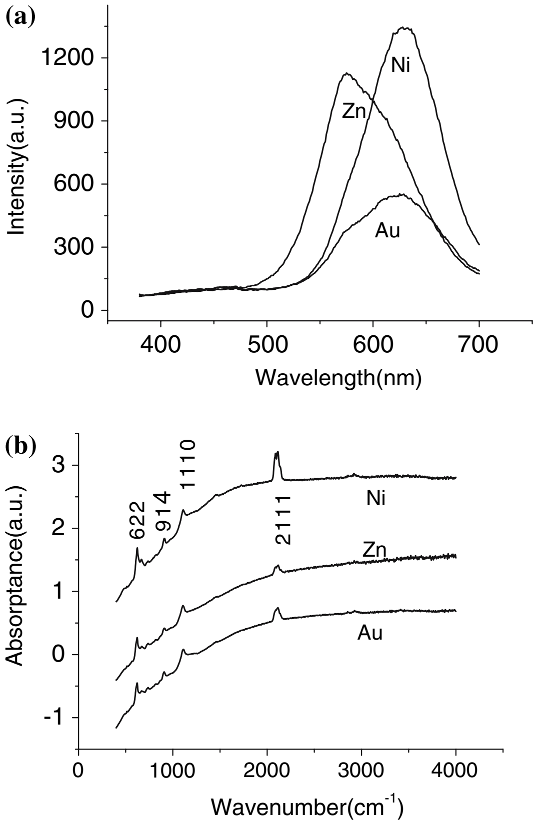

**Fig. 4** PL spectra (**a**) and FTIR spectra (**b**) of as prepared PS with different metal-aid under front illumination

PL came from defects states on PS surface and hydrogen atoms were used to eliminate irradiative centers, which were agreed with above results.

In Fig. 5, SEM images showed that etching rate was progressively decreased when the metal element varied from Zn to Ni, which was different from the results in Fig. 2. This phenomenon can be explained by the formation theory of PS. When the back illumination was used during anodic etching, the light-generated holes diffuse from silicon bulk to growing pore tip and the effect of metal element on light-generated minority carrier is negligible. When the light-generated carriers were produced by front illumination during anodic etching, thin metal film can remove light-generated minority carriers by irradiative combination process, which led to the decrease of etching rate. According with this theory, the PS with Ni aid may receive the lowest PL efficiency, but in fact the opposite result was showed in Fig. 4. It may be attributed to the hydrogen atoms on PS surface, which can eliminate irradiative centers and enhance the PL efficiency.

## Summary

PL and minority carrier lifetime of PS under back or front illumination were studied. PL may come from defect states on PS surface and hydrogen atoms adsorbed on PS surface

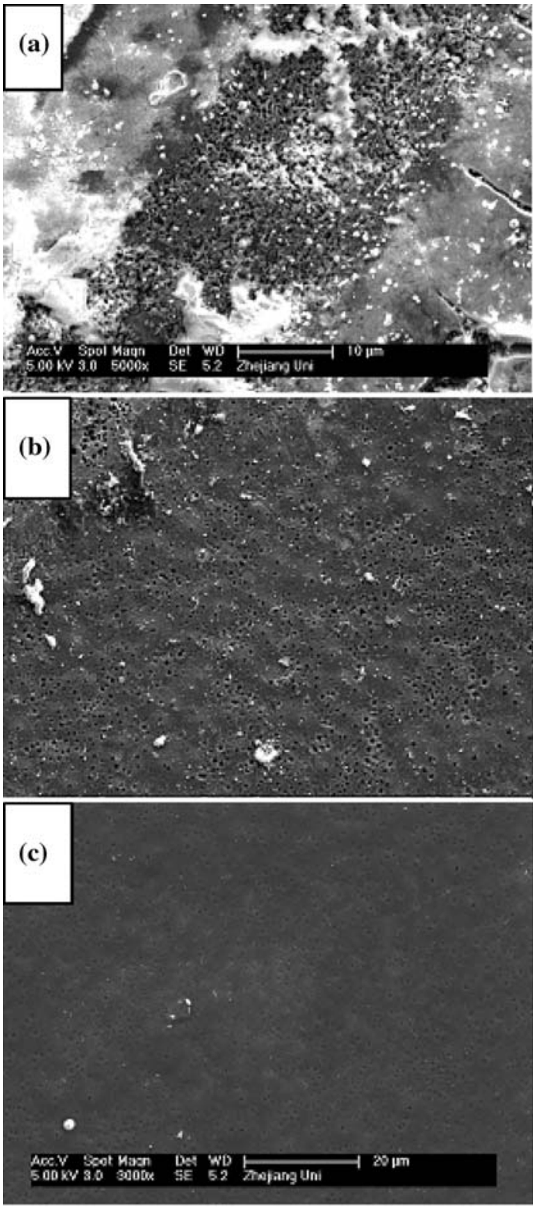

**Fig. 5** SEM images of as prepared PS without or with different metal-aid under front illumination. (**a**) Zn; (**b**) Au, (**c**) Ni

were used to eliminate the irradiative centers and enhance the PL efficiency. The introduced metal can result in different etching rate, different morphologies and different minority carrier lifetime. Furthermore, the same metal used in anodic etching showed different etching rate when PS was prepared under different illumination conditions, which can explain by formation theory of PS.

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