The Functionalization of Surface Modified Silicon

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Study in my dissertation focuses on the functionalization of surface modified silicon. The dissertation is constructed from five chapters as summarized below.

Content

In chapter 1, the review on surface modification of silicon for functionalization, particularly the importance, applications and challenges, are presented. Silicon is a material of interest in many research areas and applications. However, for some optical applications, Si is not a good choice. In order to extend the application of Si, the silicon surface is often modified to achieve higher optical absorption, stronger and more stable visible fluorescence emission and so on. Despite the fact that there has been great improvement in this research field, the remaining challenges still hinder the practical applications. One of the problems associates with the formation of porous structure when the typical surface modified Si was prepared by common electrochemical anodization. The porous surface causes difficulties in the deposition of some additional homogeneous thin metal layers which are often required to modify the electronic properties on demand for specific electronic applications. Simultaneously, the photoluminescence (PL) from such surface modified Si usually shows a single red emission with a poor stability. Therefore, the study presented in this dissertation is focused on solving these issues.

In chapter 2, preparation and formation mechanism of the columnar porous silicon (PSi) was investigated. Surface morphology of the traditional surface modified Si prepared by electrochemical anodization in conventional aqueous hydrofluoric acid (HF)/ethanol electrolyte shows an irregular porous structure which is inconvenient to form homogeneous metal film structure on its surface for practical application. One way to solve this problem is preparing the columnar Si surface. For this purpose, an oxidant containing aqueous solution was used as the electrolyte to replace the conventional one.

Various columnar PSis were obtained (shown in Fig. 1) and the prepared samples with regular columnar surface are suitable candidates to form homogeneous metal films on its surface for practical devices. This is also the first time to synthesize the columnar surface by pure electrochemical anodization.

Chapter 3 is first focused on solving the problem of PL quenching related to the columnar PSi. In order to improve the stability of PL from the prepared columnar PSi, my study proposed a feasible approach to create stable PL center by sputtering deposition of a Cu layer onto the columnar PSi at room temperature followed by aging and HF etching. This method was proposed to protect and create stable PL centers by avoiding the effect of high temperature treatment which often required in common preparation technique. Compared to the unstable red PL of anodized porous Si, the resulting Cu coated porous Si after aging and etching shows a dual PL bands at blue and yellow range with increased intensity (shown in Fig. 2). These two emissions also exhibited a good stability with negligible degradation after three months. The improvement of PL can be attributed to the surface unstable SiO that combines with the sputtered Cu, forming new Cu related defect sites and surface nanostructures. These results can extend the application field of silicon as a potential optoelectronic candidate.

![Fig. 1. The surface structures of the prepared electrochemical anodized Si.](image)

![Fig. 2. Left: comparison of photoluminescence spectra of Cu-PSi samples (2 months aged in air and HF treated the surface before sputtering) under different sputtering conditions under an excitation wavelength of 260 nm. Right: photoluminescence spectra of Cu-PSi with a sputtering time of 2 min (2 months aged in air and HF treated the surface before sputtering) under various excitation wavelengths.](image)
the surface structure. For this purpose, a nano-island structured SiOₙ (x ≤ 2)/CuₙO (x ≤ 2) composite was prepared from a Cu deposited Si wafer by electrochemical anodization in a HF and ferric nitrate electrolyte. The composition of the nano-island was consisted of Cu, Cu oxides, Si nanoparticles and Si oxides with separated distribution regions of the Cu ions and Si nanoparticle. As a result, an uncommon dual-parallel band PL at red and blue ranges with comparable intensity was observed shown in Fig. 3. The origin of the red PL is due to oxygen defects in the band gap of Si nanoparticles/Si oxides; the blue PL is the consequence of the transitions between 3d¹⁰ ↔ 3d⁹ 4s¹ of Cu⁺ and the intra d → d band transition of Cu²⁺ in the interstitial vacancies of Si oxides. Compare to the electrochemical anodized bare Si sample, the nano-island structured SiOₙ/CuₙO composite emitting a dual-PL-band is more promising for white light emitter.

Chapter 4 is devoted to utilize the columnar PSi for improvement of the terahertz (THz) emission from metal-semiconductor interface. THz emission from CuₙO (x ≤ 2)/AuCu nano thin film was studied by using the columnar PSi substrate. The results demonstrate that the THz emission from the samples on the columnar PSi was several times more efficient than that from the sample on planer Si substrate (shown in Fig. 4). Additionally, surface reflectance in the case of the PSi substrate was significantly reduced compare to that in the case of the planar one, owing to multiple reflections on the column surface. Because Si, Cu and Au are widely applied to microelectronic chip as the logical unit and intermediate layer for electronic adjustment respectively, the enhanced THz emission from CuAu composite on PSi substrate can make THz technology potentially integrates with microelectronic device.

![Fig. 3](image_url)

**Fig. 3.** (a) Fluorescence spectra of the freshly prepared nanoisland SiOₙ/CuₙO composite and anodized bare Si (the anodized bare Si was prepared by same method without Cu coating before electrochemical anodization. The emission spectra were collected at the excitation wavelength of 320 nm); (b) Fluorescence emission spectra of the freshly prepared nanoisland SiOₙ/CuₙO composite collected under different excitation wavelengths.

Finally, Chapter 5 summaries the contributions and future perspectives of my study presented in the dissertation. The successful functionalization of the surface modified Si is achieved including stable PL emission, dual PL from Si/Cu based materials and enhanced THz emission from metal/semiconductor on columnar PSi surface. The preparation methods and findings in my study contribute to the fundamental understanding on formation of columnar morphology, stabilization of PL center, creation of multiple PL emission based on modifying porous Si surface with metal and metal oxides, as well as the improvement of THz emission from the columnar PSi based composites. The results are important for the development of Si-based optoelectronic device and THz integrated microelectronics.

Nanostructured Si is a promising material in recent researches. Not only the research fields in this dissertation, but also, for example, surface enhanced Raman scattering, photovoltaic applications and LED heterojunction. The combination PSi and other optoelectronic materials have a promising future in efficient LED source.