学　位　論　文　内　容　の　要　旨

DISSERTATION ABSTRACT

博士の専攻分野の名称　　博士（工学）　　氏名　魯 旭

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Title of dissertation submitted for the degree

The Functionalization of Surface Modified Silicon

(表面修飾したシリコンの機能化)

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

In chapter 1, the review on surface modification of silicon for functionalization, particularly the importance, applications and challenges, are presented. This chapter is directed to show the problems of surface modified silicon for optical applications, and my research objective and proposed approaches to overcome these problems. 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 homogenous 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 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 synthesis 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. 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.

Secondly, the Si based white light emitting materials have been pursued in light-emitting field. However the combination of blue fluorescent Cu or Cu oxide with red fluorescent PSi in single composites always shows a single PL emission as the mutual disturbance of Cu ions and PSi. Aiming to develop the dual or multiple PL emission with comparable intensity from Cu/PSi composite, my research focused on introducing the separation between these two types of PL emission centers in the composite via tailoring the surface structure. For this purpose, a nano-island structured SiO_x (x $\leq$ 2)/Cu_xO (x $\leq$ 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-visible-band PL at red and blue ranges with comparable intensity was observed. 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 $3d^{10} \leftrightarrow 3d^9 4s^1$ of Cu^+ and the intra d $\rightarrow$ d band transition of Cu^{2+} in the interstitial vacancies of Si oxides. Compare to the electrochemical anodized bare Si sample, the nano-island structured SiO_x/Cu_xO composite emitting a dual-PL-band is more promising for white light emitter.

Chapter 4 is devoted is to utilize the columnar PSi for improvement of the terahertz (THz) emission from metal-semiconductor interface. THz emission from Cu_xO (x $\leq$ 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. 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 integrate with microelectronic device.

Finally, Chapter 5 summaries the contributions and future perspectives of my study presented in this 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.