様　式　Ｃ－１９、Ｆ－１９－１、Ｚ－１９　（共通）

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研究課題名（和文）Luminescent and electrically conductive nano-silicon for optoelectronics and photovoltaics

研究課題名（英文）Luminescent and electrically conductive nano-silicon for optoelectronics and photovoltaics

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研究成果の概要（和文）：・ポーラスシリコン（PS）の光学定数における新たなin-situ測定方法を開発した．本方法により，すべての多孔率におけるPS光学定数測定に初めて成功した；様々なHF溶液濃度におけるシリコン層の溶解速度測定ができた；PSの光溶解現象観測および解析モデルの確立ができた．
・高量子収率61％（世界記録である）のSi/SiO2ナノ粒子の作成に成功した．1-ヘキセンを用いた気相化学修飾法の開発により，PS表面のSi-H結合をより安定なSi-C結合に置換することができた．この方法は低コストで気圧制御が簡単にできるため液相化学修飾法効率的である．

研究成果の学術的意義や社会的意義
・ポーラスシリコン（PS）ナノ構造における化学・光溶解現象の観測及び解析は，シリコンナノテクノロジー分野で非常に重要な基礎研究である．これらの現象の解釈モデルの確立によりPS層のより正確な作成が制御可能となる．
・世界的な高量子効率記録を示すシリコンナノ結晶は，太陽電池やバイオマーカ分野に応用できる．これらの分野への応用は現在の我々の主な挑戦である．気相化学修飾法による安定したPS発光層の作成は，より簡便なプロセスの実現を可能とした．

研究成果の概要（英文）：A new method of determination of optical constants of Porous Si was shown. It is easy, allows for study of perfectly preserved materials and for the first time allows the study of all porosities. The dissolution rate of silicon in various HF-based solutions was achieved. Photo-etching of porous Si was also characterized experimentally and theoretically with a model. Si/SiO2 core/shell nanoparticles with world record high quantum yields (53-61%) were obtained. The same method led to quantum yields of ~ 30% for porous silicon powders. These nanocrystals were very stable and exhibited the longest lifetimes ever reported for such nanocrystals. A new method of gas-phase chemical modification of nano-silicon surface to replace Si-H bonds by more stable Si-C bonds was studied using 1-hexene. This method is easy, low-cost and allows for gas pressure control. It is much more efficient than the liquid-phase one. The resulting photoluminescence of the nano-silicon layers was well-stabilized.

研究分野：Applied Physics

キーワード：Silicon　nanocrystals　porous silicon

様　式　Ｃ－１９、Ｆ－１９－１、Ｚ－１９、ＣＫ－１９（共通）

１．研究開始当初の背景

Silicon overwhelmingly dominates microelectronics. It is also non-toxic, bio-compatible and low-cost. However, it is a poor light emitter in its bulk form. As a result, organic and other inorganic materials (e.g. GaN alloys) dominate the optoelectronic world. These materials do have limitations, such as cost, toxicity or stability issues.

Visible light emission is possible in nano-silicon due to quantum confinement (QC). Porous nano-silicon (PSi) layers offer many advantages such as low-cost, easy processing and scaling, tunable properties, and no need for vacuum technology or poisonous gases. However, so far, the luminescence has been inefficient and not stable.

２．研究の目的

Basic and applied studies will be conducted on porous nano-silicon, nano-silicon oxide, and powders. Important targets are the control of the nano-structures shape, size and surface chemistry, their luminescence (emission spectrum, lifetime, efficiency and stability). These materials could be applied to multi-color lighting, bio-imaging, sensing, and photovoltaics.

３．研究の方法

For size control by chemical and photo-chemical etching, it was necessary to understand the phenomena involved. We succeeded by using a technique allowing the monitoring of these phenomena and simulation/fitting models.

To enhance the luminescence efficiency of Si nanocrystals, we have used a particular oxidation technique allowing for the formation of very good quality surface passivation layer

For efficient stabilization of Si nanocrystals by short organic molecules, we have proposed a new method of gas-phase hydrosilylation using 1-hexene. The method is low-cost, easy to implement and very effective.

４．研究成果

(1) Etching of porous Si in HF, and optical characterizations.

Figure 1 shows the porosity-dependence of the absorption coefficient derived continuously for the first time from ~ 60% porosity to 100% porosity. The absorption results were discussed considering the Bruggeman model of effective medium approximation and other measurements from the literature, together with the effects of quantum confinement (QC) and surface states. The study also allows the determination of the dissolution rate of silicon in various HF-based solutions.

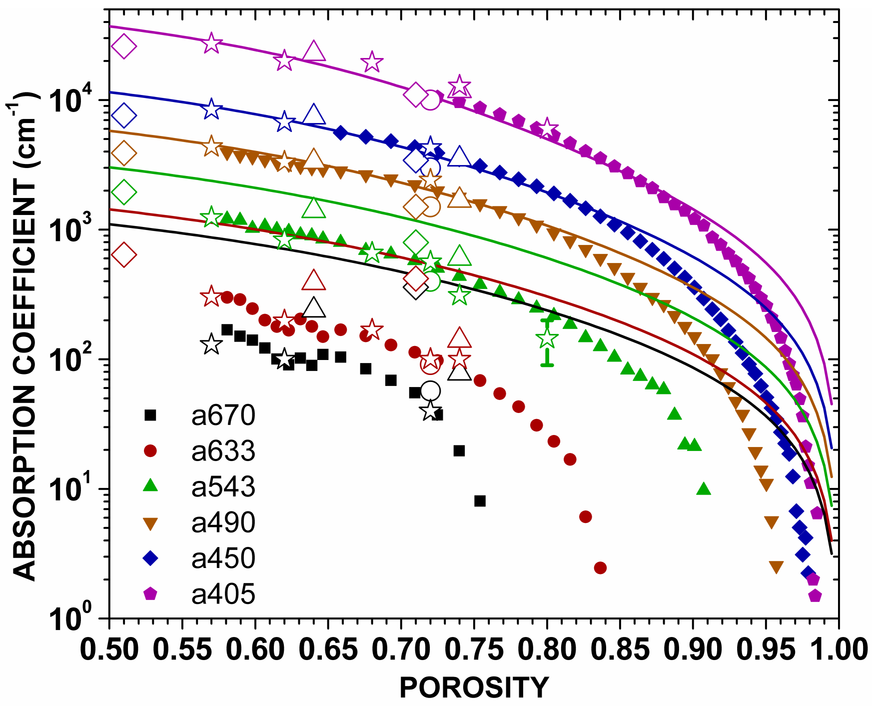

Figure 1: Absorption coefficient at different wavelengths as a function of PSi porosity. Solid symbols were obtained from our method. Hollow symbols are data from the literature or our own independent measurements (☆). Lines were obtained by using the Bruggeman model.

Photo-assisted etching of PSi in HF solution has been, so far, not well controlled and characterized. We developed a method of photoetching monitoring, and a model was developed. Two regimes were characterized, one in which the photoetch rate is limited by the supply of photo-generated holes at the Si surface, and another one where it is limited by the rate R_0 of the chemical reactions after initial hole capture, for illumination powers greater than a threshold value. R_0 was evaluated as about 0.06 Å/min. The model was used to calculate porosity profiles during photoetching.

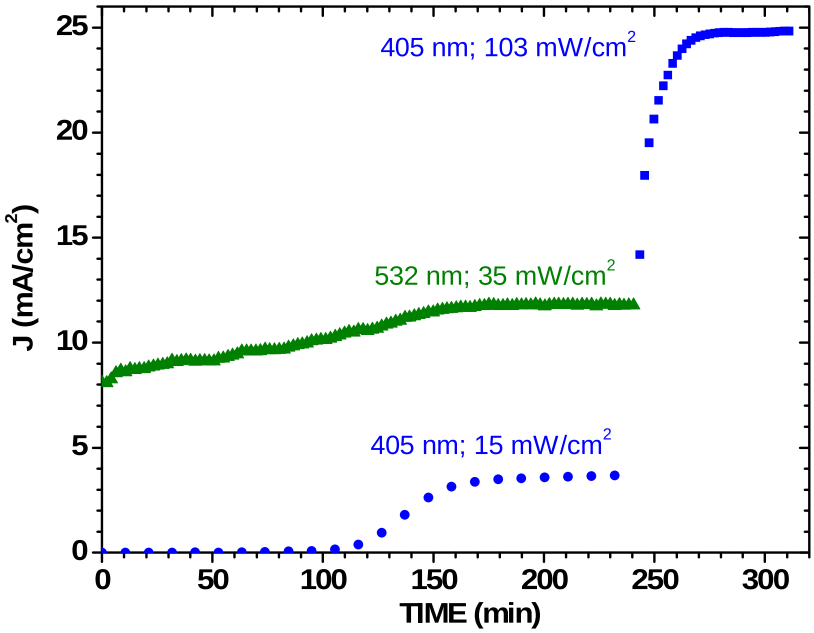

Figure 2. Photocurrent density under continuous photoetching at 532 nm, for a 5 μm-thick PSi layer (porosity 62%). Simultaneously, the photocurrent density obtained using a lower power 405 nm laser light was measured. In a second step, only the blue laser was used, at a higher power, to continue the photoetching.

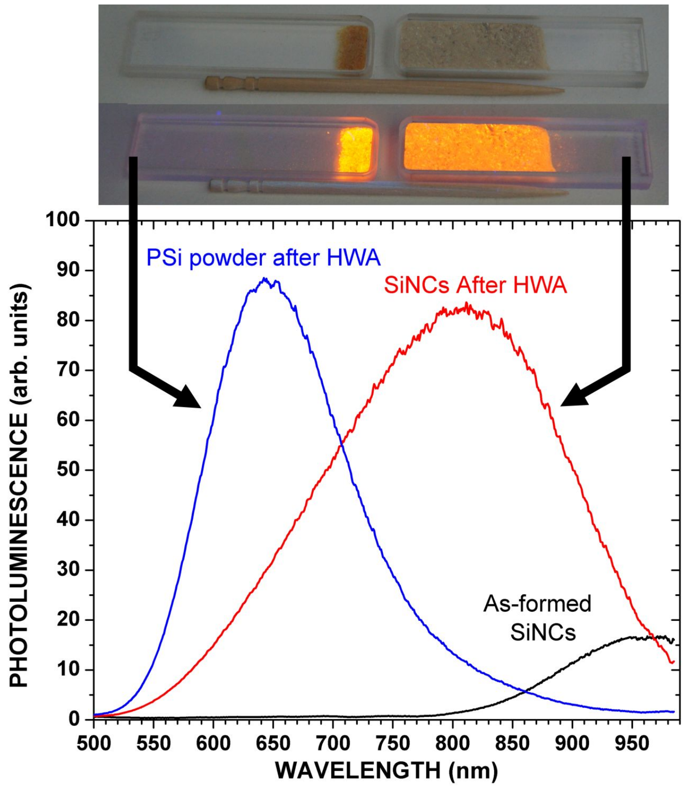

Figure 3: PL of SiNCs powder before and after oxidation, and of PSi powder after HWA. Pictures of the powders under a 365 nm lamp are shown when the lamp was off and on.

The effect of illumination wavelengths was discussed. A signature of QC in high-porosity PSi was observed, as shown on Fig.2. In a first step, PSi is photoetched at 532 nm until PSi becomes transparent at 532 nm due to QC. In a second step, photoetching was continued at 405 nm, showing PSi was not fully photoetched by 532 nm, and showing the effect of QC.

(2) Highly efficient luminescent Si nanocrystals (Figure 3).
Most of the highly efficient luminescent silicon nanocrystals (SiNCs) reported to date consists of organically capped silicon cores. Here, we report a method of obtaining Si/SiO_2 core/shell nanoparticles with very high quantum yields (53-61%). The SiNCs were very stable under continuous excitation for several hours. The lifetime at 1.5 eV was over 232 μs, the longest ever reported for SiNCs, consistent with the very high luminescence efficiency. The oxidation process we have developed allows for the growth of very good quality oxide with low defect concentration and low stress, resulting in very good surface passivation, which explains the very high quantum yields obtained.

(3) Stabilization of PSi surface with a new method.
A new method of gas-phase chemical modification of nano-silicon surface to replace Si-H bonds by more stable Si-C bonds was studied using 1-hexene. This method is easy, low-cost and allows for gas pressure control. It is much more efficient than the liquid-phase one. The resulting photoluminescence of the nano-silicon layers was well-stabilized.

５．主な発表論文等

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