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研究課題名（和文）Developing rare-earth free metal-oxide plasmonic hybrid structures for wavelength conversion and near-infraed photoelectric transfer

研究課題名（英文）Developing rare-earth free metal-oxide plasmonic hybrid structures for wavelength conversion and near-infraed photoelectric transfer

研究代表者

シンデ　サティッシュラクスマン（Shinde, Satish）

国立研究開発法人物質・材料研究機構・国際ナノアーキテクトニクス研究拠点・NIMSポスドク研究員

研究者番号：00771354

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研究成果の概要（和文）：本研究では酸化ゲルマニウムの欠陥準位励起による波長変換と、プラズモン媒介光電変換を実現するためのナノ材料開発、界面制御研究を推進した。プラズモニック金属（TiN / Au）と酸化物/窒化物（GeO2 / C3N4）の適切な組み合わせにより、実験により近赤外光誘起光電流発生と水分解を目指した光触媒化学反応を実証した。また、ゲルマニウムナノピラミッドと半導体量子ドットを光捕集アンテナとして用いたダウンコンバータ発光を見いだし、その発光増強メカニズムを解明した。

研究成果の概要（英文）：We have completed the set target to optimize the defects in oxides and examine the wavelength conversion and demonstration of a “plasmon-mediated photoelectric transfer”. With suitable combinations of plasmonic metal (TiN/Au) and oxides/nitrides (GeO2/C3N4), we demonstrated the near IR light induced photocurrent generation and photocatalytic chemical reactions for water splitting. The defect-mediated broad-band NIR upconversion is still under investigations. The work on optimization of defects in GeO2/Ge pyramids structure, NIR light induced photocurrent generation and TiN/carbon nitride composite have been presented in various conferences/meetings (S. L. Shinde et. al. IUMRS-ICAM, Aug. 2017; ISSS-8, Oct. 2017; MANA International Symposium, March 2018) and published in peer-reviewed journals (S. L. Shinde et. al. ACS Photonics 2017 (4), 1722, ACS applied materials & interfaces 2018 (10), 2460).

研究分野： Photoelectric converters and detectors

キーワード： Wavelength conversion　Plasmonic antenna　Wide band gap materials　Oxides　Defects

１．研究開始当初の背景

Photon wavelength conversion is useful in many applications such as photovoltaics, deep-tissue bioimaging, photodynamic therapy, data storage, and security and surveillance applications. In most of these applications, either lanthanide-based solid-state or organic bimolecular converters are used. While organic bimolecular wavelength converters can be as efficient as 16% and lanthanide are only about 2-5% in efficiency. Moreover, the absorption and emission wavelength ranges for these wavelength converters are fixed by the atomic or molecular energy levels yielding narrow-band emissions and are challenging to tune.

２．研究の目的

We propose a new type of *"lanthanide and molecule free"* wavelength converters: *We examine the combination of plasmonic nanostructures with the semiconductor/oxide heterojunction for the photon wavelength conversion and emission in the visible to near infrared region*. This defects mediated wavelength conversion is a novel unique approach proposed by us for applications in energy transducers such as photocatalytic reactions and thermophotovoltaic (TPV). Here, plasmonic metals such as Au or TiN (as low-cost alternative plasmonic ceramics) will be adopted to constitute the plasmonic light harvesters which also act as sources for hot carriers. Plasmonic excitation at the metal/Ge interface yields hot electrons and holes and will inject them into Ge conduction and valence bands. Subsequently, they drift into the defect levels of GeO_2 and then recombines to radiate into photons with higher energies compared to the incident photons.

３．研究の方法

The underlying aim is to develop rare-earth free metal-oxide plasmonic hybrid structures for wavelength conversion *via hot carrier generation in plasmonic antennas and subsequent recombination/light emission at the oxide/semiconductor interface and near-infrared photoelectric transfer.*

The proposed project is divided into two parts: 1) first part deals with the plasmonic wavelength converter and the other deals with 1) plasmonic charge separator for NIR photovoltaic module and catalytic reactors. The proposed work will be carried out in following steps:

４．研究成果

We have developed the design and fabrication methods for synthesis of plasmonic antenna for optimum VIS-NIR photon confinement, the wavelength conversion and plasmonic metal combine oxide/nitride for catalysis. In the proposed wavelength converter (GeO_2/Ge/TiN/Si), under illumination of longer wavelength light at plasmonic TiN and narrow band gap Ge interface, the hot carrier generated in TiN transfer to the defects containing GeO_2 through Ge, where it recombine to emit shorter wavelengths. To have wavelength conversion, the defects state in oxides plays the important role.

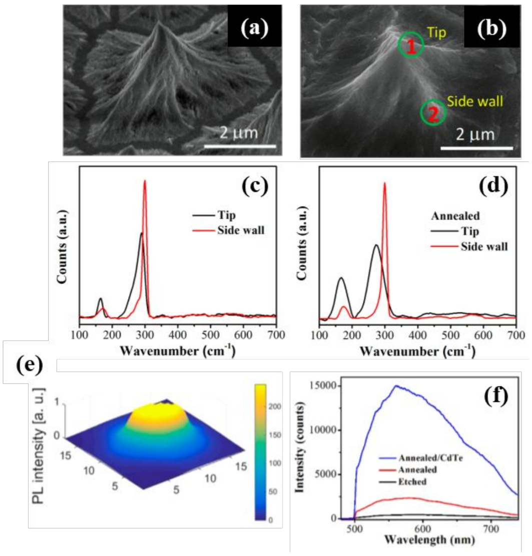

Figure 1. SEM images of (a) etched Ge wafer and (b) etched Ge wafer annealed at 400 °C for 2 h. Raman spectra of etched (c) and annealed (d) Ge wafers at different positions, respectively. (e) 3D PL mapping image of the annealed samples (f) PL spectra of an as-etched sample and an annealed sample before and after the addition of CdTe QDs. The excitation wavelength was 470 nm.

For the preliminary work on optimization of defects in GeO_2/Ge structure, we fabricated GeO_2/Ge pyramids structures on Ge wafer and studied the defects states by luminescence and Raman measurements. Figure 1a and b show the SEM images of nanopyramids of GeO_2/Ge prepared by chemically etching the Ge wafer. The Raman spectra are shown in Fig. 1c and d before and after annealing of pyramids structures confirm the tip of pyramids contains more defects compared to side walls. The Raman measurements confirmed the presence of a heavily roughened GeO_2/Ge interface. Thus, a higher density of oxygen defects would naturally be expected. To associate the defect-related luminescence to the spatial information, we performed PL imaging of the etched Ge samples. Figure 1d shows PL mapping for the annealed sample. As expected, only the tip (center) part of the pyramid-shaped region was bright (yellow color), that is, luminescent. The luminescence decreased away from the pyramid's tip, which suggests a variation in the defect density along the side wall. Surprisingly, when the Ge nanostructures were coated with CdTe QDs (Fig. 1f), the PL intensity was further enhanced remarkably. Further, this defect containing GeO_2/Ge will be combined with plasmonic nanoantenna for the realization of wavelength conversion.

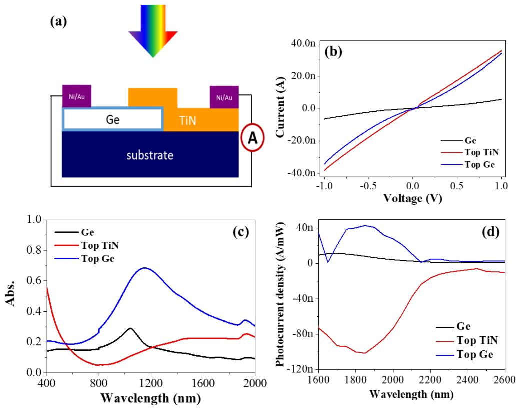

Figure 2. (a) Schematic of in-situ fabricated TiN/Ge interface for sub-band gap photodetection. (b) I-V curve, (c) Absorptance and (d) photocurrent density under illumination of NIR light for Ge film, top TiN and top Ge films.

Also, the TiN/Ge interface plays the crucial role in light absorption and plasmonic hot carrier transfer from TiN to GeO_2. We have studied the interfacial properties of TiN/Ge by measuring the photocurrent under illumination of NIR light. The planar samples that form in-situ Ge/TiN interface (Fig. 2a) are fabricated by DC sputtering technique, and the generation of photocurrent by near-infrared (NIR) light illumination is confirmed up to 2600 nm, well exceeding the absorption limit of Ge. The fabricated TiN/Ge interface form slightly Schottky contact (Fig. 2b) and shows absorption in visible to NIR region (Fig. 2c). The bare Ge file shows photocurrent for the excitations of light above the band gap of Ge and very weak or negligible photocurrent below band gap excitations. For TiN/Ge film, we observe much higher photocurrent below the band gap of Ge. Below band gap excitations, the plasmonic hot carriers generated in TiN and transfer through Ge results in sub-band gap photocurrent in TiN/Ge (Fig. 2d). This results will, therefore, facilitate the use of TiN, which is robust and inexpensive, as an alternative for photo-exciting hot carriers in NIR photodetection and in photovoltaics.

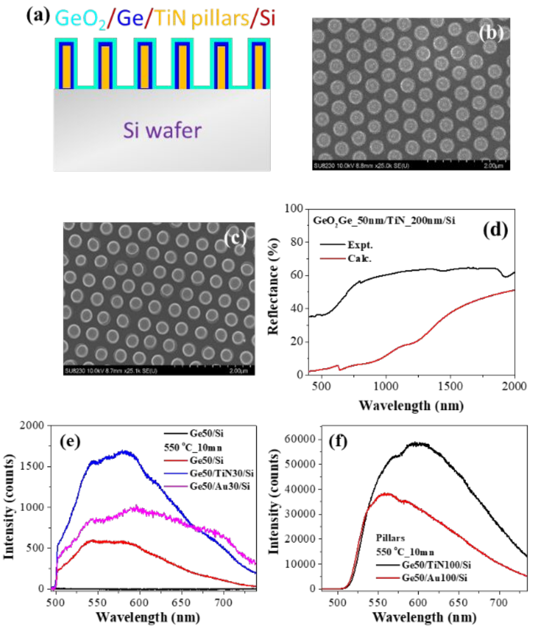

Figure 3. (a) Schematic of GeO_2/Ge/TiN pillars/Si wavelength converter. (b and c) SEM images of TiN pillars and GeO_2/Ge/TiN pillars on Si. (d) Experimental and calculated reflectance spectra of GeO_2/Ge/TiN pillars/Si. (e) PL of the thin film of Ge, GeO_2/Ge, GeO_2/Ge/TiN and GeO_2/Ge/Au. (f) PL of nanopillars of GeO_2/Ge/TiN and GeO_2/Ge/Au. The excitation wavelength was 470 nm.

Next step is to fabricate the defects-containing oxide layers on the plasmonic nanostructures and examine the wavelength converting properties. By controlling the plasmonic nanostructure size and shape, the light confinement and improvement in absorption are possible. As observed for Ge pyramids, the VIS-NIR light absorption is observed to be more than 90% compared to ~ 60% for flat film of Ge. We have successfully developed the TiN pillars with specific dimension nanostructure plasmonic antenna on Si substrate for optimum NIR confinement by colloidal lithography method (Fig. 3a). Figure 3b show the SEM images of TiN pillars antenna grown on Si substrate. On the above structure, we fabricated GeO_2/Ge structure for examining the wavelength conversion. The 50 nm Ge is coated on 200 nm diameter TiN nano pillars further heated at 550 °C for 10 mn to form defects containing GeO_2/Ge layer (Fig. 3c). All the films are well characterized to have better quality and stability. These structures show the broad absorption in NIR region (Fig. 3d). Experimental results are in good agreement with the calculated reflectance. We studied the defects in GeO_2 by luminescence measurements.

As expected, due to the narrow band gap, the bare Ge film does not show any visible luminescence on the excitation of 470 nm (Fig. 3e). When Ge film annealed in oxygen deficient condition, the defects containing GeO_2 form on Ge. This shows very weak luminescence in the visible region. The defects containing GeO_2/Ge film fabricated on TiN or Au film shows luminescence enhancement. The luminescence enhancement is observed to be ~ 3-fold and 2-fold for GeO_2/Ge/TiN and GeO_2/Ge/Au films, respectively compare to GeO_2/Ge film (Fig. 3e). The GeO_2/Ge fabricated on nanopillars of TiN and Au on Si, the luminescence enhancement is observed to be ~ 109-fold for TiN pillars and ~ 64-fold for Au pillars (Fig. 3f). The reason for very large enhancement in luminescence could be strong confinement and absorption of light and efficient transfer of excitons from plasmonic metal to defects state in GeO_2. The results of sub-band gap photodetection and hot carrier mediated luminescence enhancement suggest that under excitation of NIR light there is a possibility of hot carriers transfer from plasmonic metal to defects state in an oxide, where it recombine to emit shorter wavelengths. *The defect-mediated broad-band NIR upconversion is still under investigations.*

The next part is a demonstration of a "plasmon-mediated photoelectric transfer" with suitable combinations of plasmonic metal and oxides/nitride and near IR light induced photocurrent and chemical reactions study. For this, we have developed the Plasmonic TiN and carbon dots embedded carbon nitride composite for efficient NIR absorption and catalysis. In this work, a promising strategy to increase the broadband solar light absorption was developed by synthesizing a composite of metal-free carbon nitride−carbon dots (C_3N_4−C dots) and plasmonic TiN nanoparticles (Fig. 4a) to improve the photoelectrochemical water-splitting performance under simulated solar radiation. Hot-electron injection from plasmonic TiN NPs to C_3N_4 played a role in photocatalysis, whereas C dots acted as catalysts for the decomposition of H_2O_2 to O_2. The use of C dots also eliminated the need for a sacrificial reagent and prevented catalytic poisoning. Utilization of the TiN NPs and the incorporation of C dots into the C_3N_4 matrix led to an increase in the UV−VIS to NIR absorption over the major part of the solar spectral region (Fig. 4b), which performed better than the C_3N_4 composite with Au NPs and C dots. By incorporating the TiN NPs and C dots, a sixfold improvement in the catalytic performance of C_3N_4 was observed (Fig. 4c and d). The proposed approach of combining TiN NPs and C dots with C_3N_4 proved effective in overcoming low optical absorption and charge recombination losses and also widens the spectral window, leading to improved photocatalytic activity. Further improvement is expected through the optimization of this synergistic effect and could provide useful information toward designing visible photocatalysts for commercial applications.

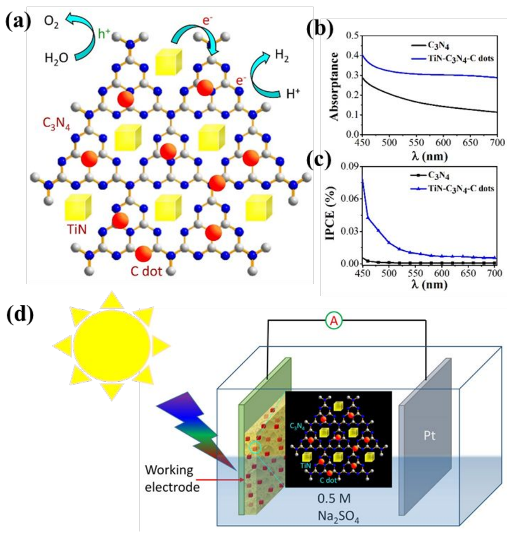

Figure 4. (a) Schematic of TiN-C_3N_4-C dots composite. (b and c) Absorptance and incident photon to current conversion efficiency (IPCE) of C_3N_4 and TiN-C_3N_4-C dots composite. (d) Schematic of photoelectrochemical cell to study the water splitting reactions.

Overall, we have completed the set target to optimize the defects in oxides and examine the wavelength conversion and demonstration of a "plasmon-mediated photoelectric transfer". With suitable combinations of plasmonic metal (TiN/Au) and oxides/nitrides (GeO_2/C_3N_4), we demonstrated the near IR light induced photocurrent generation and photocatalytic chemical reactions for water splitting. *The defect-mediated broad-band NIR upconversion is still under investigations.*

５．主な発表論文等
（研究代表者、研究分担者及び連携研究者には下線）

〔雑誌論文〕（計　２　件）
1. Satish Laxman Shinde, Satoshi Ishii, Thang Duy Dao, Ramu Pasupathi Sugavaneshwar, Toshiaki Takei, Karuna Kar Nanda, Tadaaki Nagao, Enhanced Solar Light Absorption and Photoelectrochemical Conversion Using TiN Nanoparticle-Incorporated C_3N_4-C Dot Sheets, ACS applied materials & interfaces, 4, 2018, 2460-2468.
DOI: 10.1021/acsami.7b15066
2. Satish Laxman Shinde, Thang Duy Dao, Satoshi Ishii, Li-Wei Nien, Karuna Kar Nanda, Tadaaki Nagao, White Light Emission from Black Germanium, ACS Photonics, 4, 2017, 1722-1729.
DOI: 10.1021/acsphotonics.7b00214

〔学会発表〕（計　５　件）
1. Satish Laxman Shinde, Satoshi Ishii, Tadaaki Nagao, Sub-bandgap Photodetection from Germanium/Titanium Nitride Heterostructure, MANA International Symposium, Tsukuba, Japan, 2018.
2. Satish Laxman Shinde, Thang Duy Dao, Satoshi Ishii, Li-Wei Nien, Karuna Kar Nanda, Tadaaki Nagao, Enhanced visible-light emission from Quantum dots sensitized GeO_2/Ge perfect absorptive hetero-nano pyramids, IUMRS-ICAM, Yoshida Campus, Kyoto, Japan, 2017.
3. Satish Laxman Shinde, Thang Duy Dao, Satoshi Ishii, Tadaaki Nagao, Quantum Dots Mediated Enhanced Visible-light Emission from Black Germanium, ISSS-8, Tsukuba International Congress Center, Tsukuba, Japan, 2017.
4. Satish Laxman Shinde, Thang Duy Dao, Satoshi Ishii, Tadaaki Nagao, Fabrication of Black Ge and its surface characterization, Thermo Fisher Scientific seminar, FT-IR Raman Users Forum, Tokyo Conference Center, Shinagawa, Japan, 2017.
5. Satish Laxman Shinde, Satoshi Ishii, Tadaaki Nagao, Enhancement of Broadband Solar Light Absorption and Photocurrent Increase of C3N4 Nanoparticles Combined with TiN and Carbon Nanoparticles, The 77th JSAP Autumn Meeting, TOKI MESSE Niigata Convention Center, Niigata, Japan, 2016.

〔図書〕（計　１　件）
1. Satoshi Ishii, Kai Chen, Ramu P Sugavaneshwar, Hideo Okuyama, Thang D Dao, Satish Laxman Shinde, Manpreet Kaur, Masahiro Kitajima, Tadaaki Nagao, Wiley－VCH Verlag GmbH & Co. KGaA, Materials Nanoarchitectonics, 2018, 13.

〔産業財産権〕

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〔その他〕
ホームページ等

６．研究組織
(1)研究代表者
シンデ　サティッシュラクスマン(Shinde, Satish Laxman)
国立研究開発法人物質・材料研究機構
国際ナノアーキテクトニクス研究拠点
研究者番号：00771354

(2)研究分担者
(　　)
研究者番号：

(3)連携研究者
(　　)

研究者番号：

(4)研究協力者