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Photoelectronic Sensor with Gold Nanoparticle Plasmon Antenna

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14. ABSTRACT
Proposed research of a photo-electronic hybrid device utilizing gold nanoparticles (GNPs), which are supposed to function not only as the Plasmon antenna but also as the sensing part. The photocurrent in the fabricated device, consisting of a transparent Nb-doped TiO2 channel and Au electrodes, was enhanced more than eight times at a specific wavelength with GNP arrays located between the electrodes, indicating that surface Plasmon resonance was electrically detected with the hybrid device. This result will open new doors for ultra-small biosensor chips integrated with multi-functional solid-state devices.

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Abstract:

We have proposed a concept of a photo-electronic hybrid device utilizing gold nanoparticles (GNPs), which are supposed to function not only as the Plasmon antenna but also as the sensing part. The photocurrent in the fabricated device, consisting of a transparent Nb-doped TiO_2 channel and Au electrodes, was enhanced more than eight times at a specific wavelength with GNP arrays located between the electrodes, indicating that surface Plasmon resonance was electrically detected with the hybrid device. This result will open new doors for ultra-small biosensor chips integrated with multi-functional solid-state devices.

Introduction:

Surface Plasmon resonance (SPR) and localized surface Plasmon resonance (LSPR) phenomena have gained considerable attention and currently been applied for high-sensitivity biosensors. The frequency and intensity of surface Plasmon absorption bands are sensitive to the type of material and its size, shape, and distribution, as well as to the surrounding media. Thus, the optical response of metal nanoparticles, which are functionalized with acceptors for detecting target biomolecules, informs us of the existence of tiny amount of biomolecules and their reaction kinetics in liquids. For the sensing devices, the scattered or reflected light is collected and/or guided with an objective lens and optical fibers and converted into electrical signals. In spite of the simplicity of the optical detection system, SPR and LSPR-based sensors provide very high sensitivity and have big advantages in the research fields of clinical diagnostics and pharmacology. However, the common optical detection system has definite limits in terms of miniaturization of equipment size and its integration with functional devices. In addition to the sensing devices, SPR and LSPR phenomena are applicable to optoelectronics and considered as powerful tools that boost performance of various optical circuit devices, such as waveguides and photodetectors. More recently, photodetectors with a distinctive concept have been reported: the Au/nt-Si Schottky photodetector consisting of periodically arranged identical Au nanostructures that play important roles as both Plasmon antennas and Schottky electrodes in contact with the nt-Si layer. The photocurrent in the device strongly depends on the wavelength of incident light, exhibiting the maximum photocurrent at the LSPR absorption wavelength determined by the size and geometry of Au nano-structures. This is because LSPR enhances electron-hole pair generation in Au nanostructures and hot electrons are injected into the semiconductor through the Schottky barrier to amplify photocurrent under reverse bias conditions.

Experiments, Results and Discussion

(1) New photoelectric device with gold nano particle Plasmon antenna (To be submitted to Applied Physics Letter)

In our research, aiming at direct electrical detection of plasmonic signals, we extend this concept based on Schottoky contact to the photoelectronic hybrid sensing device with a transparent semiconductor channel and Plasmon antenna. We propose a practical and simple concept of the photoelectronic hybrid device utilizing gold nanoparticles (GNPs), which are supposed to function not only as a Plasmon antenna but also as a sensing part to detect surrounding media and biomolecules. The proposed photoelectronic device is schematically shown in Fig. 1. A pair of metal electrodes is formed on a transparent semiconducting layer, and GNP arrays are arranged in the channel region between the electrodes. Fabricating the photoelectronic device involves the following essential challenges: a selective arrangement of high-density GNP arrays in the channel region, material selection, and design for channel and electrodes in order to detect photocurrent enhanced by surface Plasmon. As for GNP arrangement, we had previously developed the selective transport method for GNPs using a ferritin-based encapsulation system. As shown in Fig. 1, this ferritin-based method enables us to form high-density single-layer GNP arrays on TiO_2 surfaces.

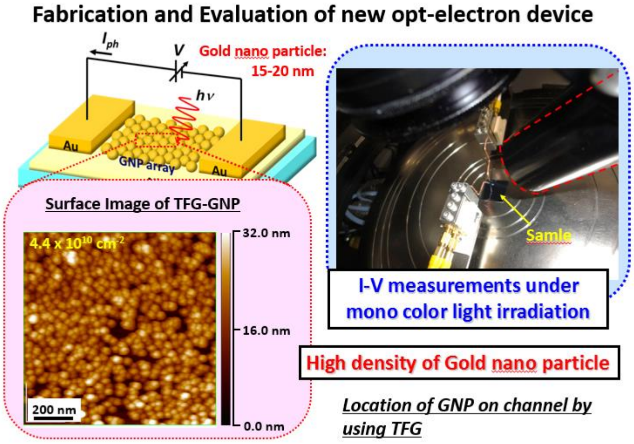

Fig.1 Schematic Image of New Photoelectric Device. A pair of metal electrodes is formed on a transparent semiconducting layer, and GNP arrays are arranged in the channel region between the electrodes

If we assume SPR is excited at the surface of Au electrode, main part of hot carrier composing photocurrent is excited at the surface of Au electrode. Then photo current amplification will be enhanced, if the distance between Au surface and AuNb-TiO2 interface forming Schottky barriers, is decreased. Therefore, by preparing sample with various Au electrode film thickness ranging from 10 to 50nm, amplification factor at each wavelength were measured as shown in Fig.2. With decreasing Au electrode thickness, photo current amplification factors were increased. When Au electrode is thick, hot carriers are generated by SPR at the surface of Au electrode, however, most of them will be inactivated until they reach Au/Nb-TiO_2 interface. On the other hand, when film thickness is thin, hot carriers by SPR will reach the interface before being inactivated, thus large photo current can be obtained. From these results, enhancement of photocurrent originating from SPR effect was experimentally demonstrated.

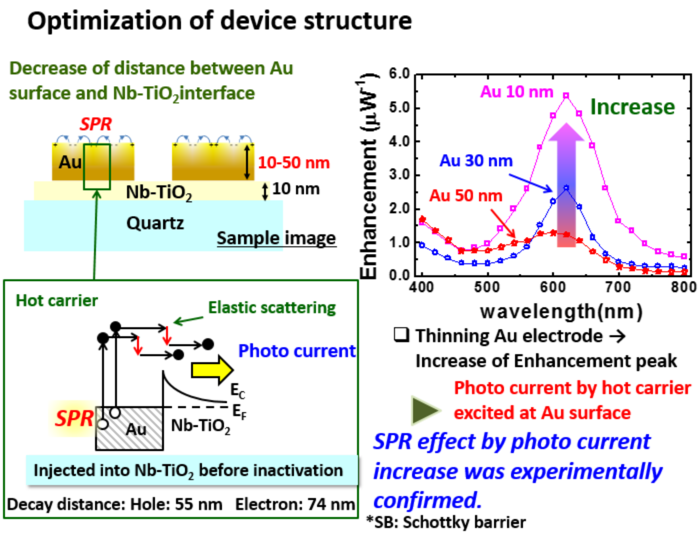

Fig.2 Mechanism of photocurrent generation. With decreasing Au electrode thickness, photo current amplification factors were increased. When film thickness is thin, hot carriers by SPR will reach the interface before being inactivated, thus large photo current can be obtained.

By decreasing Au electrode film thickness to 10nm, improvement of photo current amplification at wavelength of 620 nm was confirmed despite of using GNP. By using this optimized structure, we tried to confirm the improvement of LSPR detection by arraying TFG-GNP on the channel. Photo amplification with various wavelength is shown in Fig.3. As shown in this figure, enhancement of photo current amplification was observed by arraying TFG-GNP similarly with before the optimization. We can conclude that improvement in detection rate of LSPR signal was achieved by using optimized structure.

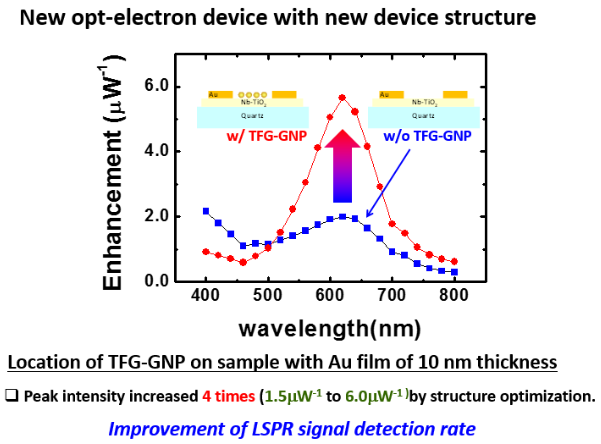

Fig.3 Photo amplification with various wavelength was measured. Enhancement of photo current amplification was observed by arraying TFG-GNP. Improvement in detection rate of LSPR signal was achieved by using optimized structure.

(2) New photoelectric device with embedded gold nano particle Plasmon antenna (To be submitted to Applied Physics Letter)

We tried to fabricate new photoelectric device using TiO_2 film with embedded gold nano particles as shown in Fig.4. By the irradiation of the light to GNP, light energy is adsorbed by plasmon effect, leading to the generation of hot carriers. These hot carriers are injected over Au/TiO2 schottoky barriers and they are detected as photocurrent. Dependence of photo current and light absorbance is coincided, thus it is concluded that light energy is converted into current.

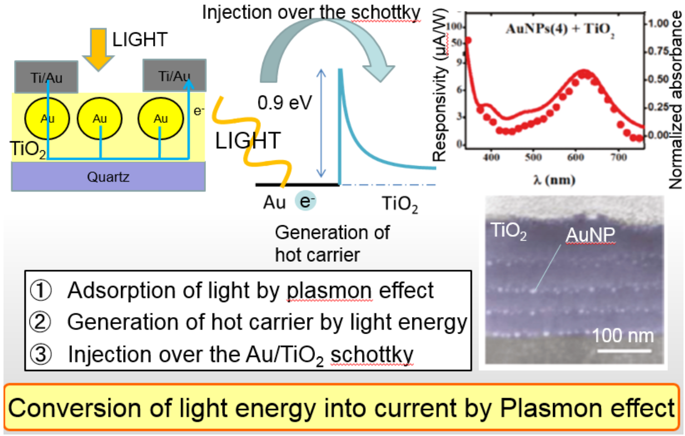

Fig.4. new photoelectric device using TiO_2 film with embedded gold nano particles. By the irradiation of the light to GNP, light energy is adsorbed by plasmon effect, leading to the generation of hot carriers.

Bio nano process is one of the unique technique for controlling nano structure by utilizing protein. We focused on the protein called ferritin. By decorating ferritin with titan precognitive peptide and gold precognitive peptide, we can array GNP on titan substrate. Feature of this method is location control and uniform dispersion (Fig.5).

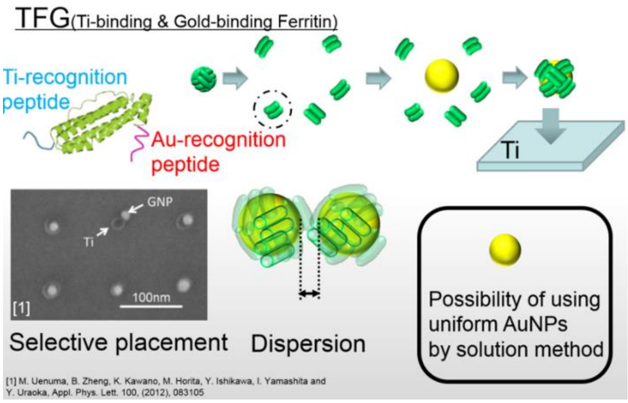

Fig.5. We focused on the protein called ferritin. By decorating ferritin with titan precognitive peptide and gold precognitive peptide, we can array GNP on titan substrate.

In order to improve plasmon antenna property, light absorption property is important. Arraying GNP and shifting the refractive index of surrounding material, change the light absorption property. To detect the change of refractive index, high light absorption and steep spectrum is required. Therefore, high density location on the substrate and uniform dispersion of GNP is strongly required. However, conventional method cannot provide nano dots with uniform size and dispersed array. Thus we employed bio nano process as shown in Fig.6. High density and dispersed GNP are arrayed on the TiO2 substrate. In spite of the size, uniformly dispersed nano dot array was obtained.

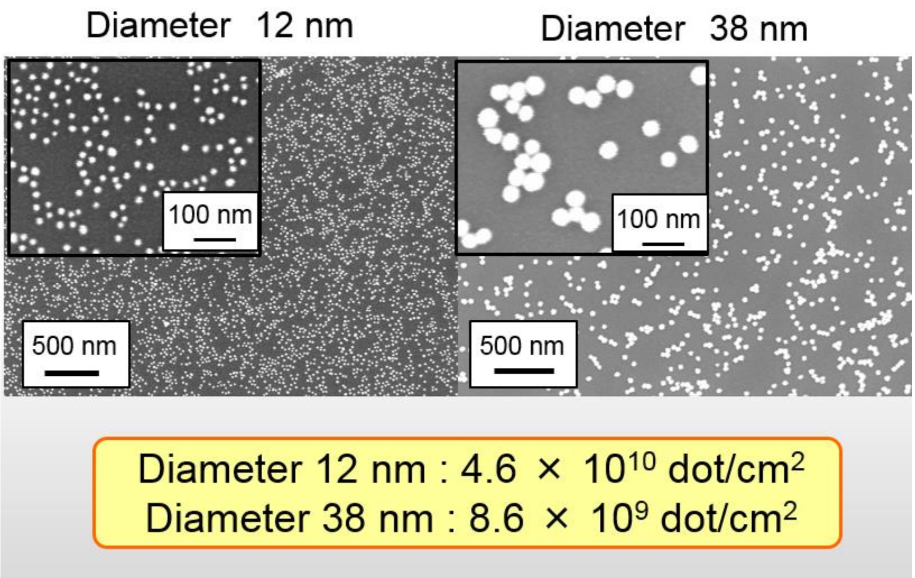

Fig.6. High density and dispersed GNP are arrayed on the TiO_2 substrate. In spite of the size, uniformly dispersed nano dot array was obtained.

By using GNP array fabricated with bio nano process, we applied them to sensing device and measured optical properties. Fabrication process of bio sensor is as follows: TiO_2 film with 15nm thickness is deposited on glass substrate, GNP is absorbed on the film. After removing outer protein by UV ozone, TiO2 is deposited again and annealed. As optical properties, reflectance and transmittance is measured. From these measurements, peaks indicating Plasmon effect can be observed at 614 nm. Next we compared the optical properties fabricated with bio nano process and conventional thermal treatment method. We confirmed narrow peak for bio nano process.

Next we measure electrical property of the sample with and without nano dots. We observed photo current at around 300 nm originating from band gap of TiO2. And another photo current peak was observed at around 600nm for the sample with and without GNP. We analyzed the peak by peak separation method. We found that this peak can be separated into 5 component and we detected photo current by Plasmon effect as shown in Fig.7. However, unfortunately this component was not remarkable.

We discussed the origin of photo current due to non-Plasmon effect as shown in Fig. 8. Energy levels corresponding to the each component of photocurrent were due to oxygen vacancy in TiO2 film. Therefore, in order to detect clear Plasmon signal, suppression of oxygen vacancy and high quality TiO2 film are necessary.

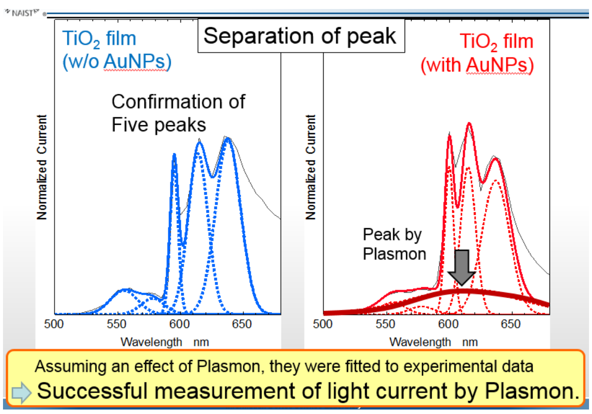

Fig.7. Photo current peak was observed at around 600nm for the sample with and without GNP. We analyzed the peak by peak separation method. We found that this peak can be separated into 5 component and we detected photo current by Plasmon.

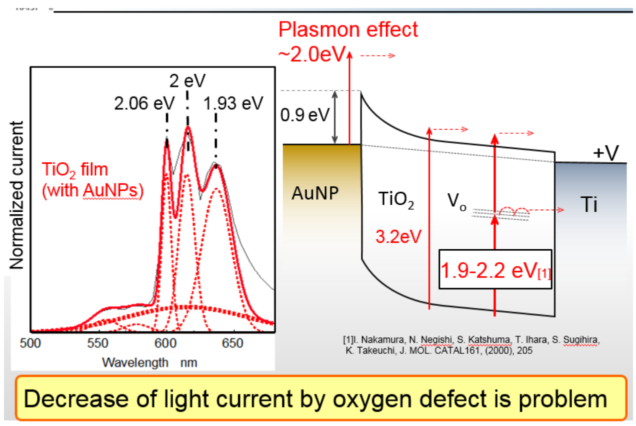

Fig.8. Origin of photo current due to non-Plasmon effect. Energy levels corresponding to the each component of photocurrent were due to oxygen vacancy in TiO_2 film.

Young Research (Yasuda) Award

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