論文の内容の要旨

Abstract of Dissertation

Near-infrared plasmon and luminescence on conductive oxide semiconductors
(導電性酸化物半導体の近赤外におけるプラズモンおよび発光)

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Oxide materials have rich history and also widely used by early humans in various forms such as paint medicinal ointment etc. In mid of the 19th century, it was started to use as oxide electronics. Especially in the 1980s, many researches were concentrated on oxide semiconductors; due to the dramatically advanced to produce oxides. Thus far, many studies have concentrated on oxide semiconductors because of various functionalities such as magnetism, optics and electronics. Many researchers have directed attention to many types of oxide semiconductors (ZnO, In_2O_3, TiO_2, VO_2 and WO_3), which possess several electronic states such as a metal, semiconductor and insulator. In particular, impurity-doped ZnO and In_2O_3 provide new insight for optoelectronics in the near-infrared region, which have been applied for photonics and medical engineering. Rare-earth ion-doped ZnO is regarded as promising for integration of a light source because light emissions are produced in the wavelength region from ultra-violet to NIR rehion. Furthermore, surface plasmon polaritons of ZnO:Ga and In_2O_3:Sn are observed in the NIR region, which plays an important role in enhancing NIR light emissions due to an increased electromagnetic field by surface plasmons.

ZnO is a semiconductor of wurtzite structure with wide band gap of 3.4eV and large exciton binding energy of 60meV at room temperature, which is much higher than that of GaN (21 meV). This makes ZnO an ideal material to realize room temperature excitonic devices. Another big advantage of ZnO is ability to grow on single crystal or even on glass substrates since its c-axis preferred orientation. Because of this c-axis orientation, higher electron mobility can be expected even on glass substrate. Thus, ZnO can be a suitable candidate for applications like SPR sensors, which uses glass prism. ZnO is available in large single crystals, therefore the epitaxy of ZnO film on native substrate leads to low concentration of extended defects. Another big advantage over standard semiconductor is that, ZnO is amenable to wet chemical etching and low temperature growth, which is particularly important in the device design and fabrication. Impurities such as Ga and Al doping into ZnO can be easily incorporated to very high carrier concentrations. Since wide band-gap energy, ZnO is the suitable host materials for the doping of luminescence centers. Moreover, ZnO is biocompatible and can be used for biomedical applications without coating.

In_2O_3 is also a transparent semiconductor with a wide band gap of 3.7 eV. Sn and F doped In_2O_3 are an excellent materials for solar cells, flat-panel displays etc, because of ability to control thickness and carrier concentration. Doped In_2O_3 has the highest conductivity metal oxides, because of its high electron mobility. This is one of the most important parameter in surface plasmon resonance. Thus optical, electrical properties of In_2O_3 are well studies as a conductive oxide in electronic industry.

Even though, oxide semiconductors have long history, commercialization of ZnO based products have been started recent years due to development of amorphous oxide semiconductors (AOSs). The first AOS thin-film transistor (TFT) was reported in 2004 and have created a new area of electronics known as 'giant microelectronics' typified by devices such as solar cells and flat-panel displays. Since poly-ZnO is known to act as an active layer in a semiconductor device even fabricated at low temperatures below 300 which is expected to replace hydrogenated amorphous silicon (a-Si:H). This thin film fabrication technique advancement gives driving force for even for consideration of surface plasmons excitation in oxide semiconductors, since it is needed to consider the fabricated thin film in wide range of substrates such as glasses. However poly-ZnO TFTs also still have many issues such as It is recognized that poly-ZnO TFTs still have many issues to be addressed, such as low mobility of charge carriers and unstable electrical properties, which are largely due to grain boundaries. Current researches in TFTs will affect the development exciation of surface plasmon in oxide semiconductors.

Recently Plasmonics is the one of the hot research topics, because it can be merged the fields of optics and nanoelectronics by confining light with relatively large free-space wavelength to the nanometer scale enabling novel devices. Thereby researchers in the field of high speed information processing are paid attention to overcome the difficulties faced in RC-delay of electronic devices and diffraction limitation in optical devices by utilizing plasmonic properties. However, the operation frequency is shifted to longer wavelength from visible frequency plasmon electric magnetic field spatial expansion of noble metal cannot be controlled. Even though, plasmonic devices are famous on subwavelength confinement, this property no longer exists for large operating wavelengths. This is the major drawback in when applying to nano-scale devices such as waveguides. Furthermore, plasmonic devices at NIR frequencies are attracted due to telecommunication and optical frequencies. However researches have to face significant difficulties due to loss encountered with noble metals. Therefore, researches on new plasmonic materials which can be alternated by noble metals are become essential. Which will useful to development of novel devices with unprecedented functionalities such as optical antennas, subwavelength waveguides, etc.

In this thesis plasmonic excitation of oxide semiconductors in optical and telecommunication frequencies are discussed as an alternative for noble metals at NIR frequencies. Since oxide semiconductors are capable to confine the plasmon electromagnetic field.

In chapter 2, the dielectric functions of ZnO:Ga and ITO are discussed, as it plays a main role in surface plasmon physics. I then extend the discussion to loss involved with surface plasmons, and compare low carrier density materials with noble metals. For a surface plasmon to exist in air, ε_1 should be less than (-1). However energy loss reaches a maximum around this dielectric value. When the operating frequency differs significantly from the plasma frequency, ε_2 becomes large, resulting in loss and a small propagation length. Therefore, a balance must be struck between maximizing the propagation length and reducing the entire losses. In conclusion, it is expected that the SPR curves in the NIR for any material will have larger FWHMs when compared with the visible frequencies.

The basic principle of a current injected emitter operated in NIR and their fabrication method was analyzed in Chap. 3. First optical properties of $Zn_{1-x}Eu_xO$ epitaxial layers were discussed, and were systematically investigated in correlation with structural analysis. Future more, emission spectra were analysed by exciting the band gap of ZnO and discussed about energy transferring process. Excitonic emissions were remarkably suppressed with increasing Eu content by the formation of a band tail at the band edge, which played an important role in activation energy transferring from the ZnO host to the Eu^{3+} ion. Strong Eu^{3+} emission was only observed at low temperatures, and the recombination process was explained by two types of nonradiative activation energies. Considering the recombination process in $Zn_{1-x}Eu_xO$ layers, excited carriers were trapped at the shallow states near the band edge, forming an electron-hole pair at low temperatures. This process produced nonradiative energy transfer to the Eu^{3+} ion through the high-lying excited levels of Eu^{3+} ions.

Surface plasmon excitation of oxide semiconductors were introduced in Chap.4.Ga doped ZnO and Sn doped In_2O_3 were selected as the plasmon materials in NIR region, since their low dielectric loss and higher carrier density. SP modes guided by ZnO: Ga layers are theoretically and experimentally studied. Clear SPR reflectivity is observed above the cutoff thickness of the *s*-mode propagated at the air-ZnO interface. In contrast, the QB mode associated with a hybrid surface mode was found in the SPR reflectivity of layers with thicknesses below the cutoff thickness. Sensor ability was also investigated in oxide semiconductors using water and glucose solutions as examples. An obvious enhancement of the absorption band due to water was confirmed when the absorption peak of water and the SPR peak overlapped. The acquired sensitivity on In_2O_3:Sn was close to that of the detection ability of Au metal-SPR, which was further discussed in regard to the spatial coherence of an SP wave.

In this thesis, the emission spectra of Er^{3+} in 1540nm exciting ZnO band gap and their coupling with localized surface plasmon of In2O3:Sn nano-particles were successfully demonstrated. Rare-earth (RE) doped materials have been investigated intensively as one of the promising optoelectronic materials, since sharp, photostable and long lived emission spectrum due to intra-4*f* transition. The luminescent centers in RE doped materials can act as an atomic emitter by pumping excitation energy. Plasma coupling emission enhancement by modifying the dielectric environment was discussed to overcome several drawbacks in these atomic emitters. The LSPR was observed in In_2O_3:Sn nano particles in NIR frequency who's diameter was 15 nm and we theoretically supported their LSPR using Mie theory.

There is a so-called transmission window of optical fiber communication at 1.5μm with a low loss allowing long distance transmission. It is a highly desired monolithic integration with complex circuits. The surface plasmon nanophotonic could address several existing challenges due to its nature involving hybrid technology at the interface of optics and electronics

Utilizing transparency in visible and strong plasmonic absorption of Indium oxide nano crystals as discussed in Chap. 5 in NIR than noble metals, oxide semiconductors can be applied to absorb the NIR heat from sun in solar cells to reduce the heating. One the other hand there is a recent trend energy harvesting in NIR by solar cells. As nearly half of the Sun's energy arrives at the earth in the near-infrared frequency range, scientists are investigated how to increase the absorbing amount of sunlight that can be harvested by solar panels for power generation. Furthermore NIR radiation is the only solar radiation that can be collected in sunny/cloudy day or at night. Organic material-based solar cells have been extensively studied due to their low-cost, simple and cost-effective processes. Plasmon-assisted light trapping in the active layer of a solar cell is employed to enhance weak absorbance of the organic photoactive layers.

Up-conversion luminescence based on multi-photon excitations is one of the important photonic research areas due to potential applications in laser technology, optical communications, storage, displays, imaging techniques, optical sensing and biological probing. Among these applications, up-conversion luminescence is extensively documented in rare-earth compounds for volumetric 3D displays. Surface plasmons enhanced NIR emission will be the light source to excite rare-earth ions to produce visible emission for display monitors. Indeed, surface plasmons in transparent oxides are the only candidates for display applications.