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Study on Refractory Thin-film Plasmonic Binary Compounds for Infrared Photothermal and Photoelectric Conversion

(高融点二元化合物薄膜における光熱および光電変換に関する研究)

The work presented in this thesis investigates new classes of non-conventional plasmonic materials which exhibit strong thermal and chemical stability compared to the conventional elemental plasmonic metals or refractory metals for applications in the energy-conversion field. The use of conventional plasmonic metals is restricted to application in the visible range and at relatively low temperatures, due to the limitations of their optical properties and their low temperature stability. The exploration of materials with both refractory and plasmonic properties beyond the visible region is required for the development of high-temperature and radiative heat transfer plasmonic applications.

In this work, we investigated the electrooptical properties of cerium hexaboride (CeB_6) and NiAl as the prototypical refractory compound materials for photoenergy application in the infrared (IR) region. According to previous simulations performed in our group, rare-earth metal hexaborides (RB_6) and NiAl are expected to exhibit large Fermi wavelength and remarkable plasmonic response in the IR region. This, together with their high melting points makes them potential candidates for high-temperature thermo-plasmonic applications such as selective IR photothermal emission or IR photoelectric energy harvesting. First, by comparing the electrooptical properties of CeB_6 films fabricated under different conditions (sputtering and electron beam deposition at different temperatures) we optimized the deposition parameters for the high quality CeB_6 films fabrication. Achieving high crystallinity and low roughness was one of the main conditions to obtain materials with good plasmonic response. CeB_6 layers deposited at high temperature on sapphire substrates present higher crystallinity and better optical properties compared to films deposited on Si, showing increased plasmonic performance. The films with the best properties achieve values comparable to the most commonly used refractory materials, like Mo or W, and the performance is comparable to one of the best plasmonic metals: Al. The advantage of CeB_6 is that it is stable against oxidation at much higher temperatures (around 800 – 1000 °C), whereas conventional plasmonic metal films present a surface pre-melting point of a few hundreds of degrees (around 300 °C for Al thin films).

To demonstrate the applicability of CeB_6 as a good material for thermo-plasmonics, different types of thermal emitter devices were fabricated. The design was optimized through electromagnetic simulations. The emission wavelength of the devices was designed to match the vibrational frequency of some of the most common gas molecules in the air (CO , H_2O) with the objective of gas sensor applications. The proposed devices include simple Gires-Tournois (GT)-type interferometric resonators and nanopatterned Wood's anomaly-based grating structures. The GT resonators exhibit a narrow emission peak with respect to the crystallinity of the CeB_6 films fabricated with different methods. Grating and disc array structures also present emission peaks at the target wavelengths.

I also studied another non-conventional plasmonic bimetallic material (NiAl) for photo-electric conversion applications. The plasmonic properties of this material were demonstrated previously in our group, however its potential for photo-electric applications was not investigated. The good optical response of this material, together with its unique two-dimensional film growth, renders NiAl an ideal electrode material for photoelectric conversion devices in combination with semiconductors. The highest potential of this material lies on the IR region of the spectra, where its optical response achieves its highest values. In this work, we characterize the optical and electrical properties of NiAl ultra-thin films (1.4 to 100 nm), and its capability as photoelectric transducer. To examine the photoresponsivity of the material, Schottky barrier devices were fabricated. The tuning of the Schottky barrier height between the metal and the semiconductor was considered under different approaches such as optimizing the annealing conditions or introducing a dielectric layer between metal and semiconductor. The photoresponse of the devices was characterized at different wavelengths, reaching the highest intensity at the target energy determined by the Schottky barrier. The results obtained in this study provide new insights for the exploration of novel IR optical functionality created with refractory binary compounds.