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Title of Doctoral Dissertation

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 conducted in this thesis analyzes the growth and properties of a novel class of highly conductive ceramic materials, cerium hexaboride. This material has been used extensively for its refractory and photothermal properties, however, its plasmonic properties and applicability remained unexplored. This material, together with another interesting bimetallic compound, NiAl, previously characterized in our research group, potentially exhibit novel functionalities and improved performances for photo-energy conversion applications. In this work we demonstrate the applicability of these two materials for high-temperature plasmonic applications in the IR region by fabricating nanostructured thermal emitters and Schottky barrier photoelectric devices.

In the first place, the main research focus was to find the optimal conditions to fabricate high-quality crystalline CeB_6 thin films in order to characterize the fundamental electrical and optical properties, particularly its dielectric function and plasmonic response. Achieving high crystallinity is required for an accurate characterization of the optical response of the material, since it can be easily affected by variations in the atomic arrangement and chemical composition, such as polycrystallinity, defects, strain or impurities. For this reason, the growth of CeB_6 thin films was evaluated under different fabrication conditions including deposition temperatures ranging from room temperature to 1100 °C on various substrates such as Si (100), C-sapphire and R-Sapphire by DC sputtering and electron beam deposition. The fabrication of epitaxial thin films in the (100) orientation was achieved by electron beam deposition at temperatures between 800 and 1100 °C, and the films fabricated on R-sapphire exhibited higher crystallinity and better plasmonic response (FOM) than the ones deposited on Si. The high-quality epitaxial films achieve FOM values superior to other common refractory materials (W and Mo) and comparable to that of Al. Therefore, due to its good plasmonic properties in the IR region and its high temperature stability, CeB_6 is a robust candidate for high-temperature plasmonic photothermal applications, including spectroscopic thermal emitters for gas sensing, material-selective heating, and thermophotovoltaic devices.

In order to demonstrate the applicability of CeB_6 thin films for plasmonic photoenergy conversion different types of thermal emitter devices were fabricated. The design was optimized through electromagnetic simulations. The proposed devices include 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, and their spectral characteristics can be tuned by modifying the design parameters of the top metal layer such as periodicity, height, and width of the grating. These results demonstrate that CeB_6 films exhibit great potential for utilization in photothermal applications such as spectroscopic infrared plasmonic sensing, and thermal emitters for spectroscopic heating and thermophotovoltaics.

In addition, another alternative plasmonic bimetallic material (NiAl) is analyzed for photoelectric conversion applications. The plasmonic properties of this material were characterized previously in our group, however its potential for photoelectric applications was not investigated. The good optical response of this material, together with its remarkable electric properties, renders NiAl an ideal candidate for photoelectric conversion devices such as photodiodes. The highest potential of this material lies in the IR region of the spectra, where its optical response achieves its highest values. Moreover, the use of typical plasmonic materials (e.g. Au, Cu) and semiconductors (Si) in this region is also limited due to the optical resonances and bandgap energies respectively. To study the photoenergy conversion capabilities of this material, the optical and electrical

properties of NiAl ultra-thin films (1.4 to 100 nm) were characterized. NiAl ultra-thin films (< 5 nm) present electrical conductivity, indicating that, even at such small thickness, the films are totally connected, demonstrating a 2D growing mechanism, instead of the common 3D island mechanism observed in many metals. The samples with a thickness of 3 nm exhibit resistivity values similar to those of the thicker layers (up to 100 nm), as a result of the good electron mobility through the film. To induce 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 work reported in this thesis contributes to the deeper understanding of the critical conditions to fabricate high quality crystalline thin films via epitaxial growth and the establishment of rare-earths hexaborides (e.g. CeB_6) as a strong candidate for plasmonic applications in the IR region of the spectrum. Further investigations consider the use of non-conventional plasmonic materials for photoenergy conversion by demonstrating the operation of CeB_6 based thermal emitters and NiAl ultra-thin films based Schottky devices. This study successfully reports the fabrication of photoenergy conversion devices based on conductive high-temperature compounds, one being a covalent-bonded system, and the other being a metallic/ionic system, however both of them exhibit highly metallic electronic properties. Based on that, the same electromagnetic design strategy can be applied to both systems while taking advantage of the unique properties of each of them to optimize the performance for specific applications.