NOVEL PLASMONIC GAS SENSORS

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CERTIFICATE

This is to certify that the thesis entitled "Novel Plasmonic Gas Sensors" being submitted by **Mr. T. Senthil Siva Subramanian** to the **Indian Institute of Technology Delhi**, for the award of the degree of ***Doctor of Philosophy*** in the Department of Electrical Engineering, is a record of bonafide research work carried out by him. Mr. T. Senthil Siva Subramanian has worked under my guidance and supervision and has fulfilled the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard. The results contained in this thesis have not been submitted in part or in full to any other University or Institute for the award of any degree or diploma.

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ABSTRACT

In this thesis, we have proposed novel plasmonic hydrogen sensors based on palladium coated narrow-groove plasmonic nanogratings for sensing of hydrogen gas at visible and near-infrared wavelengths. These narrow-groove plasmonic nanogratings allow the incident light to be coupled directly into plasmonic waveguide modes thereby alleviating the need for bulky coupling methods to be employed. We carried out numerical simulations of the palladium coated narrow-groove plasmonic nanogratings using Rigorous coupled wave analysis (RCWA). When palladium is exposed to varying concentrations of hydrogen gas, palladium undergoes phase transition to palladium hydride (PdH_x), such that there are different atomic ratios 'x' (H/Pd) of hydrogen present in the palladium hydride (PdH_x) depending on the concentration of the hydrogen gas. RCWA simulations were performed to obtain the reflectance spectral response of the Pd coated nanogratings in both the absence and presence of hydrogen, for various atomic ratios 'x' ($x \sim 0.125$ to 0.65) in palladium hydride (PdH_x). The results of the RCWA simulations showed that as the dielectric permittivity of the palladium (Pd) thin film layers in between the adjacent walls of the plasmonic nanogratings changes upon exposure to hydrogen, significant changes in the plasmon resonance wavelength as well as in the differential reflection spectra are observed. The structural parameters of these Pd coated narrow groove nanogratings — such as the nanograting height, gap between the nanograting walls, thickness of the palladium layer, periodicity of the nanogratings — were varied to maximize the shift in the plasmon resonance wavelength as well as the differential reflectance when these nanostructures are exposed to different concentrations of hydrogen (i.e. for different atomic ratios 'x' in PdH_x). These sensors

being proposed by us displayed greater sensitivity and higher differential reflectance than most of the currently available plasmonic hydrogen sensors.

Moreover in this thesis, we have demonstrated plasmonic sensing of hydrogen based on 2-D palladium-gold nanoshell cylinders. These nanostructures consist of gold nanocylinders as the core and an over-coating of a palladium shell layer that acts as a sensing layer for the detection of hydrogen. The optical simulations were performed using Rigorous coupled wave analysis (RCWA). The changes in the dielectric permittivity of palladium upon adsorbing different concentrations of hydrogen changes the reflectance spectra from these plasmonic nanostructures. We also optimized the geometrical parameters of the nanoshell cylinders such as gap and height of the nanoshell to maximize the sensitivity of these sensors.

Finally, we have proposed novel hydrogen sensors based on gold-yttrium nanogratings, with the yttrium nanogratings being capped with platinum. The gold-yttrium based nanogratings act as plasmonic waveguides that allow normal incident radiation coupled into the plasmonic waveguide modes. To understand the sensing behaviour of the gold-yttrium nanogratings to hydrogen uptake we have performed the simulations of the nanostructures using Rigorous Coupled Wave Analysis (RCWA) numerical method. As the yttrium layer absorbs hydrogen gas upon exposure, its optical properties — mainly the dielectric permittivity — changes upon absorption of the hydrogen gases. A thin layer of metallic yttrium (Y) on absorbing hydrogen gas makes a nonreversible phase transition from to yttrium dihydride (YH_2) which has a metallic phase and a higher conductivity than yttrium. On further absorption of hydrogen, yttrium dihydride (YH_2) undergoes a reversible phase transition from the metallic state to the semiconducting state (yttrium trihydride, i.e. YH_3). The changes in the optical properties influence the reflectivity characteristics of thin yttrium in the absence and presence of hydrogen, which thereby is exploited for sensing different atomic ratios of hydrogen (H/Y). In this work, the sensing of various atomic ratios of hydrogen are based on spectral interrogation method of the nanostructure. The nanostructures employed for hydrogen sensing demonstrated high detection sensitivity which is measured as a large shift in the resonance wavelength ($\Delta\lambda$) and high differential reflectance amplitude (ΔR).

सार

इस थीसिस में, हमने दृश्यमान और निकट-अवरक्त तरंग दैर्ध्य पर हाइड्रोजन गैस के संवेदीकरण के लिए पैलेडियम लेपित संकीर्ण-नाली प्लास्मोनिक नैनोग्रेटिंगस पर आधारित उपन्यास प्लास्मोनिक हाइड्रोजन सेंसर का प्रस्ताव दिया है। ये संकीर्ण-नाली प्लास्मोनिक नैनोग्रेटिंगस घटना प्रकाश को सीधे प्लास्मोनिक वेवगाइड मोड में युग्मित करने की अनुमति देते हैं, जिससे भारी युग्मन विधियों की आवश्यकता होती है। हमने कठोर युग्मित तरंग विश्लेषण (आर सी डब्ल्यू ए) का उपयोग करके पैलेडियम लेपित संकीर्ण-नाली प्लास्मोनिक नैनोग्रेटिंगस के संख्यात्मक सिमुलेशन किए। जब पैलेडियम हाइड्रोजन गैस की अलग-अलग सांद्रता के संपर्क में आता है, तो पैलेडियम, पैलेडियम हाइड्राइड (PdHx) के चरण संक्रमण से गुजरता है, जैसे कि पैलेडियम हाइड्राइड (PdHx) में मौजूद हाइड्रोजन के अलग-अलग परमाणु अनुपात 'x' (H/Pd) होते हैं। विभिन्न परमाणु अनुपात ral x '(x ~ 0.125 से 0.65) के लिए पल्लिक हाइड्राइड (PdHx) में हाइड्रोजन की अनुपस्थिति और हाइड्रोजन की उपस्थिति, दोनों में Pd लेपित नैनोग्रेटिंगस की परावर्तन वर्णक्रमीय प्रतिक्रिया प्राप्त करने के लिए आर सी डब्ल्यू ए सिमुलेशन किए गए। आर सी डब्ल्यू ए सिमुलेशन के परिणामों से पता चला है कि हाइड्रोजन के संपर्क में प्लाज़्मानिक नैनोग्रेटिंगस के आसन्न दीवारों के बीच पैलेडियम (पीडी) पतली फिल्म परतों की ढांकता हुआ पारगम्यता के रूप में, प्लासोन रेज़ोनेंस तरंगदैर्ध्य में महत्वपूर्ण परिवर्तन होता है। इन पीडी लेपित संकीर्ण नाली नैनोग्रेटिंगस के संरचनात्मक पैरामीटर जैसे कि नैनोग्रेटिंग ऊंचाई, नैनोग्रेटिंग दीवारों के बीच की खाई, पैलेडियम परत की मोटाई, नैनोग्रेट्स की आवधिकता प्लासोन अनुनाद तरंगदैर्ध्य में बदलाव को अधिकतम करने के लिए अलग-अलग परिवर्तित किया है। परावर्तन तब होता है जब ये स्ट्रक्चर्स हाइड्रोजन के अलग-अलग सांद्रण (यानी PdHx में अलग-अलग परमाणु अनुपात 'x' के लिए) के संपर्क में आते हैं। हमारे द्वारा प्रस्तावित किए जा रहे इन सेंसरों में वर्तमान में उपलब्ध प्लास्मोनिक हाइड्रोजन सेंसरों की तुलना में अधिक संवेदनशीलता और उच्च अंतर परिलक्षित होता है।

इस थीसिस में इसके अलावा, हमने २-डी पैलेडियम-गोल्ड नैनोशेल सिलिंडर के आधार पर हाइड्रोजन के प्लास्मोनिक सेंसिंग का प्रदर्शन किया है। इन नैनोस्ट्रक्चर्स में कोर के रूप में सोने के नैनोसिलिंडर्स होते हैं और एक पैलेडियम शेल परत का एक ओवर-कोटिंग होता है जो हाइड्रोजन का पता लगाने के लिए एक संवेदन परत के रूप में कार्य करता है। आर सी डब्ल्यू ए का उपयोग करके ऑप्टिकल सिमुलेशन का प्रदर्शन किया गया। हाइड्रोजन के अलग-अलग सांद्रणों को सोखने पर पैलेडियम की ढांकता हुआ पारगम्यता में परिवर्तन इन प्लास्मोनिक नैनोस्ट्रक्चर्स से परावर्तन स्पेक्ट्रा को बदलता है। हमने इन सेंसरों की संवेदनशीलता को अधिकतम करने के लिए नैनोशेल सिलेंडरों के ज्यामितीय मापदंडों, जैसे कि नैनोसेल के गैप और ऊंचाई को भी अनुकूलित किया है।

अंत में, हमने सोने-एट्रियम नैनोग्रैटिंग पर आधारित हाइड्रोजन सेंसर प्रस्तावित किया है, जिसमें प्लैटिनम के साथ एट्रियम नैनोग्रैटिंग्स को कैप किया गया है। सोने-एट्रियम पर आधारित नैनोग्रैटिंग प्लाजमोनिक वेवगाइड के रूप में कार्य करते हैं जो प्लास्मोनिक वेवगाइड मोड में सामान्य घटना विकिरण को युग्मित करने की अनुमति देते हैं। हाइड्रोजन उत्थान के लिए स्वर्ण-एट्रियम नैनोग्रेटिंगस के संवेदन व्यवहार को समझने के लिए हमने आर सी डब्ल्यू ए संख्यात्मक पद्धति का उपयोग करके नैनोस्ट्रक्चर के सिमुलेशन का प्रदर्शन किया है। जैसे कि युट्रियम परत के संपर्क में आने पर हाइड्रोजन गैस अवशोषित हो जाती है, इसके ऑप्टिकल गुण हाइड्रोजन गैसों के अवशोषण पर बदल जाते हैं। हाइड्रोजन गैस को अवशोषित करने पर धातुयुक्त एट्रियम की एक पतली परत एट्रियम हाइड्राइड से एक अपरिवर्तनीय चरण संक्रमण बनाती है, जिसमें धात्विक चरण और एट्रियम की तुलना में उच्च चालकता होती है। हाइड्रोजन के आगे अवशोषण पर, एट्रियम हाइड्राइड धातु अवस्था से अर्धचालक अवस्था से प्रतिवर्ती चरण संक्रमण से गुजरती है। ऑप्टिकल गुणों में परिवर्तन हाइड्रोजन की अनुपस्थिति और उपस्थिति में पतली एट्रियम की प्रतिबिंबितता विशेषताओं को प्रभावित करते हैं, जिससे हाइड्रोजन (एच/वाई) के विभिन्न परमाणु अनुपातों को संवेदन के लिए शोषण किया जाता है। इस कार्य में, हाइड्रोजन के विभिन्न परमाणु अनुपातों की संवेदन नैनोस्ट्रक्चर की वर्णक्रमीय पूछताछ विधि पर आधारित हैं। हाइड्रोजन सेंसिंग के लिए नियोजित नैनोकणों ने उच्च पहचान संवेदनशीलता का प्रदर्शन किया, जिसे अनुनाद तरंगदैर्ध्य और उच्च अंतर परावर्तन आयाम के रूप में मापा जाता है।

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