# Surface plasmon resonance aided analysis of quantum wells for photonic device applications 

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## H I G H L I G H T S

- Fabrication of c-axis oriented ZnO thin film based quantum well structures has been carried out using Pulsed laser deposition technique
- 2D-FDTD simulations have been employed to study the electromagnetic fields at metal-dielectric interfaces for the designing of QW structures
- SPR based analysis of QW structures with different well width has been performed and its analogy with PL studies has been reported.
- Electro-absorptive behaviour of the QW towards the surface plasmon field leads to a pronounced dip in the SPR reflectance


## A R T I C L E I N F O

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#### Abstract

The present report aims at analyzing the quantum well (QW) structures using the highly sensitive surface plasmon resonance (SPR) technique in Otto configuration. The optical properties of ZnO and Ni doped ZnO ( NiZnO ) based QW structures grown using Pulsed laser deposition technique are investigated. An optimal value of QW width ( 8 nm ) is deduced from the SPR study for maximum charge carrier confinement which is in coherence with the photoluminescence (PL) studies conducted on the same QW structures. The metal-dielectric interfaces were modelled primarily for the design of QW structures to be analysed experimentally. The mechanism behind the coupling of QWs with SP excitation has been proposed theoretically and experimentally to substantiate the results of PL and SPR studies. The variation in the SPR curves observed as a function of the QW width can be attributed to the interaction of evanescent SP field originating at the $\mathrm{Au} / \mathrm{QW}$ interface and electroabsorptive behaviour of QWs towards the SP field.


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## 1. Introduction

Semiconductor devices integrated with mesoscopic structures exhibit enhanced quantum efficiency compared to the conventionallydesigned devices. Low dimensional structures, such as quantum wells (QW), quantum wires and quantum dots (QD) exhibit characteristic optical properties which have revolutionized the field of photonic devices [1,2]. Significant resources have already been invested for increasing the extraction efficiency of optical devices by employing the principles of quantum confinement [3,4]. The optical response of such low dimensional systems is strongly correlated with the refractive index of the charge confining layers, which can be further tuned by optimizing the dimensions of the constituent layers [5-8]. A comprehensive analysis of the structural and optical properties of the quantum confined

[^0]systems is thus, crucial for strategizing solid state device structures of technological importance.

Thus far, optoelectronic applications have been the chief motive for a major chunk of research on QW structures of oxide and nitride systems [9-11]. Zinc oxide is the most widely employed II-VI semiconductor in the field of photonics, owing to its remarkable structural and optical properties [12,13]. ZnO based QD/QW structures in particular have gained attention in the field of UV Photodetectors and emitters over the last few decades [14-16]. As far as deposition techniques are concerned, Pulsed Laser Deposition (PLD) is a powerful and well-established technique for the realization of thin films with controlled stoichiometry and multi-layered structures with abrupt interfaces. A number of reports are available on the growth of ZnO based thin films, nano-rods, quantum wells etc. for optical device applications [17-19]. Thus, in the present communication, ZnO and NiZnO based thin films and QW structures have been realized using PLD.

Here, it is important to recognize that various research groups have reported laterally enhanced quantum confinement in QWs when coupled with surface plasmons (SPs) [20]. SPs are quanta of resonant collective oscillations of conduction electrons at the metal-dielectric interface which display a high degree of spatial and spectral dispersion upon interaction with electromagnetic fields [21]. SPs have played a pivotal role in enhancing the quantum efficiency of various photonic devices such as solar cells, LEDs, photovoltaic devices etc. [22-26]. The excitation of SPs mediated by Attenuated Total Reflection (ATR) was first explained by Otto [27]. Constrained by the need to establish wave vector matching between the incident light and SPs, grating based or prism-based coupling mechanisms are predominantly adopted [21]. When a p-polarized beam impinges at a prism, placed in close proximity of a metal-dielectric interface, such that the incident angle $\left(\theta_{c}\right)$ is greater than the critical angle, $\theta_{c}$ (at which total internal reflection occurs), wave vector matching condition is fulfilled [21] and an evanescent wave is launched as per the following condition [28].
$k_{s p}=k_{\text {inc }} \eta \sin \theta_{\text {inc }} \quad \theta_{\text {inc }}>\theta_{c}$
where, $k_{s p}$ refers to the real part of SP wave vector, $k_{\text {inc }}$ is the wave vector corresponding to incident light, $\eta$ is the refractive index of the prism. Following a simplistic experimental approach for surface plasmon excitation, Kretschmann and Otto configurations in prism coupling mode are the most exploited geometries [29,30]. Contrary to the much explored Kretschmann configuration, the Otto ATR configuration is better suited to examine the optical properties of epitaxial dielectric thin films where a lattice matched substrate is a pre-requisite for their growth. The absence of a thickness constraint for the dielectric layer under Otto configuration enables it to provide a reliable and non-destructive solution to examine the optical properties of heterostructures for photonic devices.

Thus, beyond the realms of fundamental interest, it will be encouraging to explore the highly responsive nature of SPs to study the quantization effects in QWs. Conventionally, optical characteristics of QWs are studied using photoluminescence studies, which usually involve low temperature measurements. On the contrary, Otto-SPR is a highly sensitive tool to monitor slightest of changes in the vicinity of the plasmonic metal layer, even at room temperature. Additionally, the reflectance data in SPR can be utilized to estimate important optical parameters like complex refractive index and dielectric constant of the system. Tamn et al. (1993) reported photo-signal enhancement in AlGaAs diodes positioned in Otto configuration and attributed the observed photoresponse to the excitation of surface plasmon polaritons at the Al-air interface. The reflectance data was modelled to estimate the optical parameters of the constituent layers [31].

To the best of our knowledge, no reports are available on the utilization of Otto-SPR technique for the analysis of QW structures. The present communication is aimed at exploring the potential of SPR as a reliable alternative to probe the optical characteristics of multilayered geometries like QWs, at room temperature. A series of optically anisotropic NiZnO based QW structures have been grown on sapphire substrate and analysed using angular interrogation method in Otto (prism-air gap-metal-dielectric) configuration. The quantum electrodynamic coupling between SPs and QWs has been investigated as a function of varying quantum well width and an optimal value of QW width has been deduced for good optical efficiency.

## 2. Experimental details

Quantum well structures of undoped ZnO and NiZnO thin films were prepared using Excimer laser (Make: Coherent, $\lambda=248 \mathrm{~nm}$, Fluence $=$ $1 \mathrm{~J} / \mathrm{cm}^{-2}$ ) assisted Pulsed Laser Deposition (PLD) technique on transparent (0006) sapphire substrates. The substrates were cleaned in boiling trichloroethylene (TCE), followed by ultrasonication in acetone and trichloroethylene. Solid state route processed mechanically robust ceramic targets ( 25 mm dia.) of ZnO and NiZnO were prepared via ball
milling of mixed powders in respective proportions. The resultant powders were calcined at $800^{\circ} \mathrm{C}$ and subsequently pressed into pellets, which were sintered at $1100^{\circ} \mathrm{C}$ temperature. Deposition of all the layers in PLD were performed at $400^{\circ} \mathrm{C}$ substrate temperature under $100 \% \mathrm{O}_{2}$ gas ambient. An oxygen pressure of 30 mTorr was maintained during the entire deposition. The respective ceramic targets were ablated at a laser repetition rate of 5 Hz . The processing parameters involved in the deposition of QW layers using PLD technique are listed in Table 1.

The thickness of the individual constituent layers was estimated prior to the deposition of the QW structures. The thickness of the samples was measured using stylus-based thickness profiler (Dektak 150, Veeco) and correspondingly the number of laser shots was calculated to achieve the desired thickness in PLD. Initially a ZnO layer was grown on sapphire substrate followed by the growth of QW active layer (NiZnO). Five QW structures were prepared, employing different QW width (6 to 14 nm ). In all the samples, the QW active layer ( NiZnO ) was capped with ZnO film, which served as a spacer layer. The exact dimensions of all the layers are described in the subsequent section "Design of Quantum well geometry". The complete QW structure ( $\mathrm{ZnO} / \mathrm{NiZnO} / \mathrm{ZnO} /$ Sapphire) was coated with 30 nm thin gold (Au) layer using thermal evaporation technique under a high vacuum of the order of $5 \times 10^{-6}$ Torr. The processing parameters involved in the deposition of QW layers using PLD technique are listed in Table 1. It may be noted that the Ni doping in NiZnO thin films was kept fixed at an optimal value of $5 \%$, calculated based on the results from preliminary tests. 5\% Ni doping in ZnO resulted in a slightly lower optical band gap value ( 3.16 eV ) as compared that obtained for undoped ZnO $(3.28 \mathrm{eV})$ thin film. Additional details regarding thin film optimization are included in the supplementary data.

X-Ray Photoelectron Spectroscopy (XPS) was carried out in an ultrahigh vacuum ( $2 \times 10-10 \mathrm{mbar}$ ) XPS system (Make: Omicron). Monochromatic Al K $\alpha$ X-ray radiation (Energy: 1486.6 eV , accuracy: 0.1 eV ) was employed for probing the core levels (CLs) of the as-grown thin films. The structural analysis of the prepared QW structures was carried out using X-Ray Diffractometer ((Rigaku, Ultima IV) in $\theta-2 \theta$ mode, and the emission characteristics of the QW samples were studied using Photoluminescence (PL) spectroscopy employing monochromatic $(\lambda=280 \mathrm{~nm}) \mathrm{Ar}+$ Laser integrated system (LabRAM, HORIBA Jobin Yvon). The optical band gap of the samples was estimated using UVvisible spectrometer (Lambda 35, Perkin Elmer).

A laboratory assembled surface plasmon resonance (SPR) setup has been exploited to study the characteristics of prepared QW structures ( $\mathrm{ZnO} / \mathrm{NiZnO} / \mathrm{ZnO} /$ Sapphire). A BK-7 glass prism (refractive index, $n_{0}=1.517$ ) was affixed to a precision XYZ $\theta$ rotating stage for angular interrogation studies using He-Ne Laser $(\lambda=633 \mathrm{~nm})$. Au/ZnO/ $\mathrm{NiZnO} / \mathrm{ZnO} /$ Sapphire samples were mounted in Otto configuration in the vicinity of the hypotenuse face of glass prism having a fixed air gap as shown in Fig. 1(a). The schematic of the experimental SPR set up used in the present work to study the QW structures is shown in Fig. 1(b). The highly intense p-polarized laser beam was made incident on the glass prism at an angle $(\theta)$ greater than the critical angle $\left(\theta_{c}\right)$ to optically excite the non-radiative surface plasmon (SP) waves on the respective metal-dielectric interfaces. The motion of the rotating stage was controlled precisely using an automated driver which allows rotation of the prism table with step size of $0.001^{\circ}$ in both clockwise and anticlockwise direction. A highly sensitive optical power meter (Make:

Table 1
Deposition parameters for the growth of ZnO and NiZnO films by PLD.

| Processing Parameter | Value |
| :--- | :--- |
| Target | Ceramic target of ZnO and $5 \%$ Ni doped ZnO |
| Growth pressure | 30 mTorr in $100 \% \mathrm{O}_{2}$ gas |
| Substrate temperature | $400{ }^{\circ} \mathrm{C}$ |
| Laser fluence | $1 \mathrm{~J} / \mathrm{cm}^{2}$ |
| Repetition rate | 5 Hz |
| Target-substrate distance | 5 cm |

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