Title of the Thesis: **"Studies on photophysical properties of pristine and nanocomposite thin films based on sol-gel $TiO_2$"**

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## Abstract

The thesis entitled "**Studies on photophysical properties of pristine and nanocomposite thin films based on sol-gel $TiO_2$**" deals with two photophysical properties namely photoluminescence and photodetection properties of $TiO_2$ based nanocrystalline thin films. $TiO_2$ being a wide band-gap (~3.0 -3.2 eV) material is getting remarkable attention in various fields of applications due to its several unique properties like great thermodynamic stability, non-toxicity, low corrosion, and low cost. As $TiO_2$ has a very defect rich chemistry, the intrinsic and extrinsic defects present in $TiO_2$ cause appreciable change in the photoluminescence and photodetection properties. Therefore, engineering the surface defect states is very crucial to get significant modification of the mentioned properties. Here in this thesis work, easy and low-cost sol-gel technique has been used to prepare $TiO_2$ films followed by various post-growth treatments such as thermal annealing, vacuum annealing, UV curing to tune the surface defects and their concentration. Due to large band-gap, $TiO_2$ in general is ultraviolet (UV) light active and visible light blind. Among the various strategies adopted to get visible active $TiO_2$, incorporation of noble metals (Au, Ag, Pd, Pt) in $TiO_2$ is very beneficial and convenient way as these noble metal nanoparticles exhibit a unique property. The interaction of visible light with these noble metal nanoparticles results in the collective oscillation of free electrons in nanoparticle lattice in resonance with the electromagnetic field of light called surface plasmon resonance (SPR). Therefore, plasmonic Ag-$TiO_2$ nanocomposite film is synthesized to get visible photoactivity in this work. To study the defect states in $TiO_2$ like other semiconducting materials, doping is one of the well-known processing steps though the impurity incorporation into $TiO_2$ films has already achieved successfully using doping during growth or by diffusion, a controllable doping is still difficult. In such cases, post growth doping via ion implantation can be an effective way where also the accumulation of doping impurities on the surface of the $TiO_2$ due to excess surface energy can be avoided. Therefore, in this work, Li doped $TiO_2$ is synthesized to study the defects and their effect on the above said photophysical properties. With the above-mentioned motivation, the work embodied in this thesis has focused mainly on two aspects:

(i) Studies on photophysical properties of pristine sol-gel grown $TiO_2$ nanocrystalline thin films via various post-growth treatments

(ii) Studies on the photophysical properties of $TiO_2$ based nanocomposite films and the evolution of defects in doped $TiO_2$ films via ion implantation

The entire thesis consists of total eight chapters. The chapter wise contents are given below:

The chapter 1 provides a concise general introduction of $TiO_2$ material and its advantages over other wide band-gap semiconductors followed by the motivation and organization of the thesis.

A brief status review on the published works dealing with enhanced photophysical properties of $TiO_2$, $TiO_2$ based nanocomposite, and doped $TiO_2$ has been presented in the chapter 2.

Chapter 3 consists of two sections. (i) Detailed descriptions of the deposition methods, and (ii) various types of characterization techniques particularly those used for this thesis work have been discussed in this chapter.

The influence of various post-growth annealing processes on the defects of sol-gel grown $TiO_2$ thin films has been investigated in the chapter 4. It has been observed that annealing in air followed by a rapid cooling process offers an efficient method to achieve a stronger UV emission and reduced visible emissions giving the highest UV to visible emission ratio value. The correlation between various types of surface defects formed due to different post-growth treatments with the visible emissions occurred in the films has been analysed thoroughly in this chapter.

In the chapter 5, highly efficient UV photodetection property of nanocrystal assembled $TiO_2$ films via defects tuning has been discussed. An extremely high UV-to-visible rejection ratio of $1.7 \times 10^3$ and photo-to-dark

current ratio of 1.2 x $10^4$ under 10 V bias and 10 μW incident light power in a simple lateral photoconductive geometry have been observed for UV cured $TiO_2$ film. This study also explains the influence of intrinsic defects like $Ti^{3+}$, oxygen vacancy ($V_O$) as well as surface adsorbed $O_2$, OH species on the UV photodetection properties of $TiO_2$. A photo-to dark-current ratio of ~$10^4$ under as low as 1 V bias condition and 10 μW incident UV light reveal that simple sol-gel processed films followed by a post-growth UV curing can be promising candidate for efficient UV photodetector without any device fabrication.

UV to visible broad band photodetection property of plasmon assisted Ag-$TiO_2$ nanocomposite film has been presented in the chapter 6. In this study, various thicknesses of Ag nanoparticles on the sol-gel grown $TiO_2$ has been deposited and their photoresponse under various wavelengths of incident light has been rigorously discussed. For 1 nm thick Ag layer on $TiO_2$, unprecedently high photo-to-dark current ratio of $10^7$, $10^5$ and $10^4$ under 350 nm, 680 nm and 550 nm light illuminations have been observed. It has been concluded that the plasmonic hot carriers play a crucial role in the highly enhanced visible photodetection property of Ag-$TiO_2$ nanocomposite film which depends on the Ag nanoparticle size.

In chapter 7, both photoluminescence and photodetection properties of Li doped $TiO_2$ films prepared via post growth ion implantation method has been illustrated. It has been observed that creation of more acceptor levels defects upon Li ion fluence of $1x10^{14}$ causes violet emission. Then with increasing the fluence, probably due to creation of nonradiative recombination pathways, the violet emission has been disappeared. The enhanced visible emission has been noticed for higher fluence sample indicating formation of more defects like $V_O$ and $Ti^{3+}$ related states.

A list of up-to-date references relevant to the topics of the chapter has been included at the end of each chapter.

Finally, in the chapter 8, a summary of the important results stemming out from this thesis work has been listed followed by a future scope of the work.

D Basak 13/12/2022

Signature of the Supervisor (with Seal)

Dr. D. Basak, Ph.D.
Professor
Department of Solid State Physics
Indian Association for the
Cultivation of Science
Jadavpur, Kolkata - 700 032

Sulakshana Mondal 13/12/22

Signature of the candidate