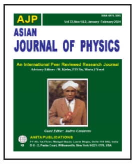

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Near-field scanning optical microscopic studies for surface plasmon polariton in heavily doped nitride nanostructures

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Near-field scanning optical microscopy (NSOM) plays a key role in achieving optical resolution beyond the so-called diffraction limit and studying the properties of the plasmonic materials. The present report reviews the principle of near-field scanning optical microscopy and its different modes of operation. In addition, NSOM is extensively utilized to study the plasmonic properties of metals, graphene, and heavily doped semiconductors. The applications of NSOM in plasmonic materials is also reviewed. The advantage of NSOM in generating surface plasmon polaritons is especially emphasized.

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1 Introduction

Conventional optical microscopy is limited by the abbe's diffraction limit. In other words, the spatial resolution achieved by the optical system is greater than or equal to $\lambda/2$, where λ is the wavelength of light used [1,2]. The above mentioned value of spatial resolution is achievable with an objective lens with the highest numerical aperture (N.A). Consequently, the maximum achievable spatial resolution with green light (~ 500 nm) is 250 nm. Thus, conventional optical microscopy cannot distinguish the objects separated by less than 250 nm. It is worth mentioning that the nanostructure's size and separation are less than or equal to 100 nm. Hence, conventional optical microscopy gives the ensemble information about these nanostructures. In a similar line, optical spectroscopy is also limited by the diffraction limit as it also uses a similar lens system and wavelengths of light. In other words, microanalysis cannot be done with a spatial resolution of less than 250 nm.

The spatial resolution of the optical system ($R = 0.61\lambda/N.A$) can be improved by reducing the wavelength of light. Unfortunately, the wavelength of light cannot be reduced indefinitely because of limitations arising from the lens system, and moreover, the conventional optical system mostly relies on visible light. In 1928, Synge proposed an idea to overcome the diffraction limit [3-5]. The Synge idea involves imaging the sample surface point by point with a sub-wavelength aperture. The resolution achieved by this method depends on the size of the aperture rather than the wavelength of light. The only bottleneck condition to realize the experimental setup at that time was to keep the aperture within the near-field of the sample surface ($\leq \lambda$). After the discovery of atomic force microscopy (AFM), the near-field distance between the sample and aperture can be controlled using the AFM feedback mechanism. Near-field scanning optical

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microscopy (NSOM) was realized with the combination of optical microscopy and AFM. The NSOM is also called scanning near-field optical microscopy (SNOM) [2,6].

This study provides an overview of the fundamental instrumentation utilized in NSOM and delves into the theoretical principles that underlie the high-resolution capabilities of NSOM. Various types of NSOM are also discussed in detail. Additionally, recent reports employing NSOM for optical imaging were further examined. Furthermore, the basic modes of surface plasmons were briefly outlined, and the contribution of NSOM to the study of plasmonic materials was elaborated upon.

2 Near-field scanning optical microscopy (NSOM): Instrumentation and Theory

2.1. Apertured NSOM

As mentioned earlier, the critical issue in achieving high resolution is positioning the probe in the near-field distance. NSOM exploits the AFM feedback mechanism to control the near-field distance. In the case of aperture-based NSOM, laser light is squeezed or collected through the subwavelength apertures. The resolution, in this case, is determined by the size of the aperture. The NSOM typically operates in two modes: Reflection and collection. The schematics of both modes are depicted in Figs 1a and 1b, respectively. In reflection mode, the light emanating from the aperture is raster scanned over the sample using the AFM feedback mechanism. Subsequently, scattered light is collected using the high numerical aperture objective lens in the far-field. The optical image of the scanned region is constructed by the scattered intensity at each point. The resolution achieved in the apertured NSOM is limited by the size of the aperture. However, because of the low throughput, size cannot be reduced beyond a certain limit. The typical size of the aperture is in the range of 50-100 nm. The apertured probes are typically coated with the metal aluminium to arrest the leakage of light. The apertured probes are fabricated using optical fibers. The optical fibers were tapered to get subwavelength apertures. The tapering was done by two well-known methods, such as heating and pulling, and etching [7-9].

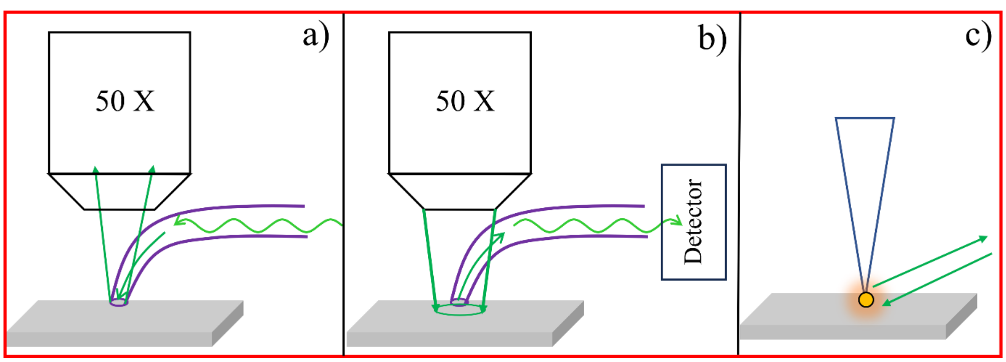

Fig 1. Different modes of apertured NSOM: (a) Reflection, (b) Collection, (c) Scattering type NSOM.

2.2 Scattering NSOM

The limitation of apertured probes lies in their maximum achievable resolution. However, this constraint can be circumvented by employing scattering-type NSOM probes. Scattering-type probes consist of sharp dielectric or metallic tips, where, upon illumination with light, light confinement occurs near the sharp tip due to the lightning rod effect (Fig 1c). This confinement is on the scale of the sharp tip's size, allowing for resolution depending on the tip's size, which can theoretically be reduced indefinitely. Metallic tips are preferred for scattering-type probes due to their high carrier density, enabling surface plasmon resonance (SPR) induction that further enhances electromagnetic field confinement and intensity around the tip. The primary drawback of scattering probes is the need for additional modulation techniques to eliminate background light [2].

3.3. Theory of high resolution of NSOM

The high resolution of NSOM stems from the confinement of light. Heisenberg's uncertainty principle elucidates this phenomenon, where the spatial confinement (Δx) of light is inversely proportional to the spread of spatial frequencies (Δk_x), expressed as $(\Delta x).(\Delta k_x) \geq 1/2$. This relationship implies that the strong confinement of photons leads to an increase in the spread of spatial frequencies and, consequently, a reduction in the wavelength of light. The in-plane wave vector ($k_{||}$) can be increased more than the total wave vector (k_o) by making the perpendicular component imaginary ($-|k_z|$) [9]. This results in an electromagnetic wave known as an evanescent wave, which possesses a broad spread of in-plane wave vectors but lacks propagative behavior in the perpendicular direction. Imaging with evanescent waves enables resolution beyond the diffraction limit [2,6,7,9,10].

Evanescent waves can be generated through various means, including subwavelength apertures, confinement of light near sharp tips, total internal reflection, and surface plasmon polaritons (SPP). Imaging with SPP at its resonance frequency can lead to the realization of a super lens or perfect lens. Subwavelength apertures or sharp tips facilitate the propagation of high spatial frequencies beyond the free space wave vector. For instance, the spatial frequencies near the aperture of size 'a' (where $a << \lambda$) possess the spatial frequencies in the range of $1/k$ …….$1/a$. Additionally, the high resolution of NSOM can be attributed to slow light. Slow light, with a lower wavelength compared to free space light, can be achieved through evanescent waves or SPP confined along the metal and dielectric interface. These mechanisms collectively contribute to the enhancement of resolution in NSOM imaging [2,7].

3 Surface Plasmons

Surface plasmon refers to the collective oscillation of conduction band electrons that are excited by electromagnetic waves. This phenomenon can manifest in two main ways: localized surface plasmon resonance (LSPR) and propagating surface plasmon polaritons (SPPs) [10]. LSPR occurs when the size of nanoparticles is significantly smaller than the wavelength of the exciting light, leading to a uniform electric field experienced by the nanoparticles. However, the condition for the observation of LSPR is that the dielectric function of the material (ε_m) and the surrounding medium (ε_d) should have opposite signs ($\varepsilon_m = -2\varepsilon_d$) [11]. Due to the abundance of free electrons in metals, surface plasmon resonance is most prominently observed in metal nanoparticles, as they readily fulfill the conditions required for activation of SPR. LSPR induces the confinement and enhancement of an electric field around the nanoparticle surface [11]. Surface-enhanced Raman spectroscopy (SERS) exploits the LSPR phenomenon, leading to a significant enhancement in the Raman scattering cross-section [12].

SPPs, on the other hand, are propagating electromagnetic waves that travel along the metal and dielectric interface confined to the interface region. These waves are evanescent in nature, meaning that the field strength decreases exponentially perpendicular to the interface. One of the most significant applications of SPPs is their ability to confine and guide light in sub-wavelength structures, effectively overcoming Abbe's diffraction limit. This property has led to the utilization of SPP propagation in sub-wavelength nanostructures to develop nanophotonic devices and optical nano-connectors. LSPR can be excited by free space electromagnetic waves, but SPPs cannot be sensitized due to momentum mismatch. Specifically, the momentum of SPPs is always higher than that of free-space electromagnetic waves [10]. Overcoming this momentum mismatch requires special techniques such as grating and total internal reflection at a prism. Additionally, evanescent waves can easily excite SPPs due to their higher spatial frequencies compared to free-space electromagnetic waves. Therefore, NSOM plays a crucial role in studying SPPs [2,6,10].

4 Applications of NSOM

4. 1. High-resolution optical imaging of III-nitride nanostructures

Sivadasan *et al* studied the near-field light-matter interaction of AlGaN nanowires using the apertured NSOM (MultiView 4000; Nanonics, Israel) [13]. NSOM measurement was carried out with an aperture of size 150 nm. A 532 nm (2.33 eV) laser excitation was used for the NSOM imaging. The near-field distance was controlled using a tuning fork-based normal force AFM feedback mechanism. The near-field scattered light was collected and directed towards a single photon counter using a long working distance of 50X. A typical field emission scanning electron microscopy (FESEM) image of AlGaN nanowires is shown in Fig 2a. The AlGaN nanowires were grown using chemical vapor deposition (CVD) via vapor-solid-liquid (VLS) mechanism [13]. The FESEM shows the well-dispersed AlGaN nanowires with a size of around 125 nm (Fig 2a). In addition, tiny spherical particles observed in the FESEM image were attributed to Au catalyst nanoparticles (Fig 2a). Figures 2b and 2c show the topographic image and its corresponding 3D representation, respectively. Figures 2d and 2e show the NSOM image and its corresponding 3D representation, respectively. The NSOM images clearly show nanowire, which has a size beyond the sub-diffraction limit. Interestingly, an Au nanoparticle with a size of 20 nm was also detected using the NSOM image. The transparency of the nanowire feature is attributed to the defect absorption of an excited laser [13].

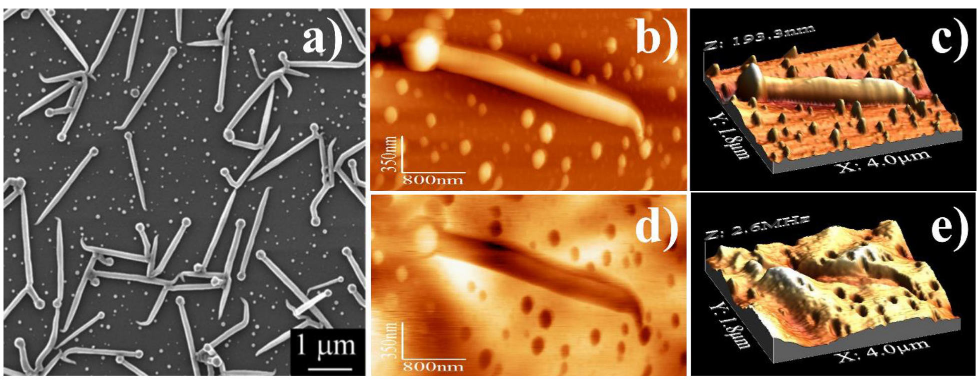

Fig 2. (a) FESEM image of well-dispersed AlGaN nanowires, (b) AFM image of AlGaN nanowire, (c) 3D representation of AFM image, (d) NSOM image of AlGaN nanowire (e) 3D representation of NSOM image. (Reproduced from Ref [13], with the permission of RSC Publishing).

Similarly, Parida *et al*, imaged the GaN nanowires using the NSOM. Here, the NSOM imaging was carried out with an aperture probe size of 150 nm [14]. Figure 3a shows the topographic image of GaN nanowires grown on Si substrate using the CVD method via the VLS mechanism. The size of the GaN nanowires was found to be in the range of 10-60 nm (Fig 1c). The nanowires make it difficult for conventional optical imaging to image these nanowires because of their small size. However, interestingly, the corresponding NSOM image shows the distribution of nanowires similar to the topographic image (Fig 1b). In other words, the nanowires are imaged optically using NSOM. The lowest size of nanowire detected using the NSOM is 10 nm, which is far below the diffraction limit [14].

4.2 Generation of surface plasmon polaritons using NSOM

Metals are the most studied plasmonic materials because of their abundant free carrier density [2,11]. However, metals suffer from high ohmic losses due to electron-electron scattering and inter-band absorption. Heavily doped semiconductors have been explored for plasmonic applications to mitigate limitations for the metals [15,16]. NSOM plays a crucial role in characterizing the plasmonic materials, especially SPPs. As mentioned earlier, NSOM is one of the techniques to overcome momentum mismatch to generate the SPPs [10]. The SPPs were generated in metal films and graphene using near-field scanning optical microscopy [17-19]. Recently, Madapu *et al* studied the near-field light-matter interaction of InN nanostructures using NSOM [20]. The study was carried out over the samples with and without surface electron accumulation. The NSOM images of InN nanostructures without surface electron accumulation provide high-resolution optical imaging. Interestingly, NSOM images of InN nanostructures that possess surface electron accumulation show the resonance behavior. Figures 4a and 4d show the topography and corresponding NSOM images of nanostructures with surface electron accumulation. The resonance behavior with enhanced light intensity around the nanoparticle was clearly observed (Fig 4d). Interestingly, fringes were observed in one of the NSOM images of InN nanostructures with surface electron accumulation (Fig 4e). The observed fringes were attributed to the generation of SPPs. The wave nature of these fringes was confirmed from the observation of interference of generated SPPs in clustered InN nanostructures (Fig 4f). The observed resonance behavior in Fig 4b stemmed from the lack of SPPs propagating area. The origin of SPPs was attributed to the 2D plasmon nature of the surface electron accumulation [20].

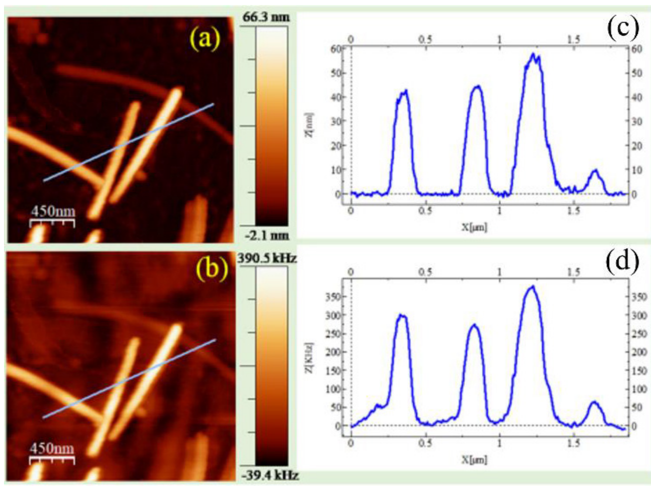

Fig 3. Topographic image of GaN nanowires (a) and its corresponding NSOM image (b). Line profile of topographic (c) and NSOM image (d) taken along the line shown in corresponding images. (Reproduced from Ref [14], with the permission of AIP Publishing).

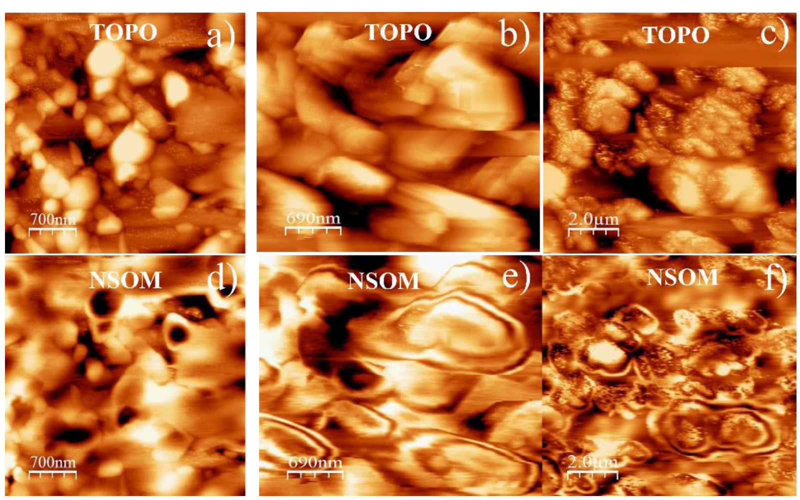

Fig 4. (a–c) Topographic image of InN nanostructures with surface electron accumulation and (d-f) corresponding NSOM images. (Reproduced from Ref [20], with the permission of IOP Publishing).

Nitrogen deficient titanium nitride (TiN_x) is one of the emerging heavily doped plasmonic materials in the IR to the visible range [21]. The carrier density of TiN_x is readily controlled using sputtering parameters. As TiN is a refractory material, it can be used in high-temperature plasmonic applications. Gadalla *et al* studied the near-field optical properties of the TiN_x films deposited on MgO substrate using the sputtering [21]. The sputtered films have shown the SPPs resonance frequency in the range of 775-825 nm. SNOM was employed to study the near-field optical properties of TiN_x film in the collection mode with different laser excitations, 775, 800, and 825 nm. Figure 5a-5c shows the SNOM images excited with 775, 800, and 825 nm, respectively. The SNOM images clearly show the fringes, which represent SPPs. The fringes stem from the interference between SPPs and the transmitted beam. The wavelength of SPPs was found to be 742 nm, 765 nm, and 791 nm for the excitation of 775, 800, and 825 nm, respectively.

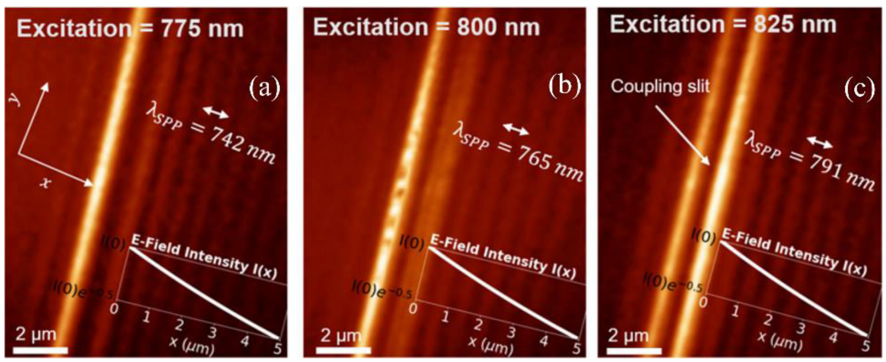

Fig 5. SNOM images of TiN film with different excitation (a) 775 nm (b) 800 nm and (c) 825 nm. Reproduced from Ref [21] with the permission of Optica Publishing).

5 Conclusion

In conclusion, our study provides a comprehensive overview of near-field scanning optical microscopy (NSOM) and its applications in pushing the limits of optical imaging resolution. We discussed the basic modes of NSOM operation, including reflection and collection, highlighting their respective roles in imaging. Furthermore, we examined various probes utilized in NSOM, considering their advantages and limitations. Additionally, we delved into the role of NSOM in characterizing surface plasmons. Our exploration extended to recent advancements where NSOM has demonstrated remarkable capabilities in imaging beyond the diffraction limit. Notably, studies have showcased the detection of 10 nm semiconducting nitride nanowires, underscoring the potential of NSOM in high-resolution imaging tasks. Furthermore, our discussion extended to the exciting realm of surface plasmon polariton (SPP) generation using NSOM, particularly in heavily doped semiconducting nitride materials like InN and TiN. Overall, our review underscores the pivotal role of NSOM in advancing our understanding of nanoscale phenomena and its potential to drive innovations across multidisciplinary domains.

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