

Bimodal Plasmonic Color Filters Enable Direct Optical Imaging of Ion Implantation in Thin Films

Catherine Sadatnajafi, Eugeniu Balaur,* and Brian Abbey*

Optical metamaterials offer precise control over the properties and interactions of light at the nanoscale, attracting interest in many new fields of research including chemical and molecular sensing, magnetic antennas, and photovoltaic elements. By utilizing the phenomenon of extraordinary optical transmission (EOT) plasmonic devices enable the detection of minute changes in the local, near-surface, dielectric properties of materials, opening up a wide range of different applications. Characterization of the optoelectronic properties of ultra-thin films is of paramount importance for a wide range of electronic applications including integrated circuit production. However, it is often extremely difficult to achieve using conventional imaging techniques. Here, it is demonstrated that plasmonic color filters can be used for the direct optical imaging and characterization of ion implantation in thin films. A model system consisting of variable doses of gallium ions implanted within titanium oxide thin films is used. It is observed that the ion implantation dose leads to a variation in the measured plasmon resonance spectra, which can be further enhanced through the use of bimodal nanopixel arrays. Using Monte Carlo simulations and the Maxwell-Garnett relation, the observed plasmon resonance spectra in terms of the gallium ion implantation dose is quantitatively interpreted.

1. Introduction

Direct detection of local changes in the dielectric properties of nanometer-thin films is important for a wide range of electronic applications.^[1–17] Ion implantation is routinely used in integrated circuit production and new approaches to characterizing ion implantation doses are continuously being researched and have attracted significant interest.^[18] Techniques such as impedance spectroscopy^[19] and ellipsometry^[20] have been

previously employed to try and probe the optoelectronic properties of thin films as a function of implantation fluence. However, plasmonic color filters offer a simple and direct alternative means for non-destructively characterizing these samples optically. Optical plasmonic sensors are particularly useful in the case of very thin films where techniques such as secondary ion mass spectrometry (SIMS) or time-of-flight (ToF)-SIMS are currently used to study dopant profiles.^[21]

Here we describe and demonstrate the direct visualization of ion implantation in a thin film (titanium oxide, TiO₂) based on analysis of the brightfield optical images and plasmon resonance spectra generated by bimodal plasmonic color filters. By measuring the optical output for these devices at two different polarization states, the relative sensitivity of the plasmon resonance transmission spectra to ion implantation can be assessed and optimized. We note that because this technique requires the device to be fabricated on top of the

sensor it cannot be easily applied post-fabrication. Instead the sensor needs to be incorporated as a substrate for calibration of the ion implantation during device production.

In this paper the behavior of the local Refractive Index (RI) of a TiO₂ film, placed within the evanescent field of a plasmonic device, is used to investigate the effect of doping using gallium ions (Ga⁺). Examination of the critical parameters involved in this process allows us to determine values of the optical constant and extinction coefficient for the ion-implanted TiO₂.

Previously bimodal plasmonic nanopixel arrays combined with polarization control have shown great promise as both color filters and chemical sensors.^[6,7,22,23] The increased versatility and dynamic range of bimodal plasmonic devices offers even greater levels of sensitivity than single mode devices for converting small changes in the samples' dielectric constant into significant modifications of the measured transmitted spectrum of the device. Shifts in resonant peak position, peak height, and peak width can be modelled based on the device parameters and incident spectrum in order to quantitatively characterize the sample.^[6]

Due to their wide electronic bandgap semiconductors such as TiO₂ and ZnO have a range of applications and exhibit high optical transmittance in the visible and near-infrared range, excellent photocatalytic properties, and large dielectric constants.^[24] The presence of dopants significantly influences both the chemical and physical properties of these materials,

C. Sadatnajafi, Dr. E. Balaur, Prof. B. Abbey
Australian Research Council Centre of Excellence for Advanced
Molecular Imaging
Department of Chemistry and Physics
La Trobe Institute for Molecular Science (LIMS)
La Trobe University
Victoria 3086, Australia
E-mail: e.balaur@latrobe.edu.au; b.abbey@latrobe.edu.au

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including modifying their magnetic and optical properties as well as their photocatalytic activity. For example, Ga ion doped TiO₂ has been used as an industrially important catalyst for selective oxidation. In addition, by tuning the TiO₂ bandgap ($E_g = 3.0$ to 3.2 eV) it is possible to create waveguides and photonic crystals and alter its photosensitivity.^[25] Previous investigations have shown that reducing the bandgap through doping TiO₂ with either metal or non-metal ions can lead to enhanced optical absorption, specifically, in the visible region.^[26] Additionally, recent works studying Ga ion implantation of ZnO nanostructures have demonstrated that doping has a significant impact on their thermal conductivity reducing it by around an order of magnitude^[27] which can be advantageous for the thermoelectric effect. Given the possibility of performing in situ measurements we anticipate that the method presented here could be useful for correlating the optical properties of the sample with changes in the electrical or thermal properties of the film.

Until recently, Ga ion implantation was used to achieve a narrower TiO₂ bandgap.^[28] It has been experimentally shown that the carrier concentration in TiO₂ increases as a function of the implantation dose, this in turn has a strong effect on the refractive index of implanted TiO₂. A higher concentration of impurities can make the configuration of the bandgap more stable and can improve the light absorption performance inducing a redshift (decreased bandgap).^[26] However, beyond a critical level of doping, further increases in the density of ion impurities do not have a significant impact on the bandgap and consequently the optical absorption does not change.^[28,29] In principle, the permittivity (dielectric function) of hybrid materials is a complex function because of the polarizability of the dielectric/metal matrix. The electric permittivity describes how strongly an external electric field polarizes the charge carriers within a given material. The optical response of a non-homogeneous, complex medium, can be characterized in terms of its electric permittivity, $\epsilon(\omega)$, described by

$$\epsilon(\omega) = \epsilon_\infty - \epsilon'(\omega) + i\epsilon''(\omega) \quad (1)$$

For each material ϵ_∞ is the contribution due to the bound electrons and is approximated as a constant value, whilst $\epsilon'(\omega)$ and $\epsilon''(\omega)$ represent the real and imaginary part of the dielectric function, respectively. The complex function of electric permittivity is a frequency dependent function. It is crucial to consider both the real and imaginary parts of this function together because, according to the Kramers-Kronig relation, they exhibit an interdependency.^[30,31] The real part of the equation describes how strongly an external electric field can polarize the material whilst the imaginary part describes the ohmic losses due to electron-electron interactions and inter-band electronic transitions.^[32–35] The link between the electric permittivity and refractive index can be derived from Maxwell's equations as

$$\epsilon(\omega) = n'(\omega)^2 = (n(\omega) + ik(\omega))^2 \quad (2)$$

where $n'(\omega)$ is the frequency dependant complex refractive index which characterises the optical properties of the material with $n(\omega)$ and $k(\omega)$ the real and imaginary components respectively.^[36,37] The coupling of light with the electronic structure of metamaterials is described by the equations governing the

surface plasmon (SP) modes; this includes both long-range surface plasmon polaritons (SPPs) and localized surface plasmons (LSPs). Other plasmon related phenomena include Wood-Rayleigh Anomalies (RA) which can be used to determine the values of the real component of the refractive index.^[38–45]

2. Experimental Section

All of the plasmonic devices used in this work were fabricated by using focused ion beam (FIB) lithography using a 30 kV Ga ion source and a 9.7 pA current. An important part of the quality control for fabrication of a given batch of devices was ensuring uniformity across the array. We evaluated the array uniformity both using high-resolution SEM imaging of different area of the array pattern and also by collecting optical spectra at different points on the array to ensure that the optical output was the same everywhere on the device to the resolution of the spectrometer (≈ 1 nm). 50 nm thick TiO₂ devices were deposited by electron beam evaporation. Ga ions were implanted into the TiO₂ films using the FIB at an acceleration voltage of 16 kV at a range of different doses with a focused ion beam radius of 5 nm.

To experimentally determine if bimodal plasmonic arrays could be used to detect Ga ion implantation, nine areas of varying Ga ion implantation dose were created using a FIB system (see Figure 1A). For each implantation area, the beam was raster-scanned in a square pattern in order to achieve a homo-

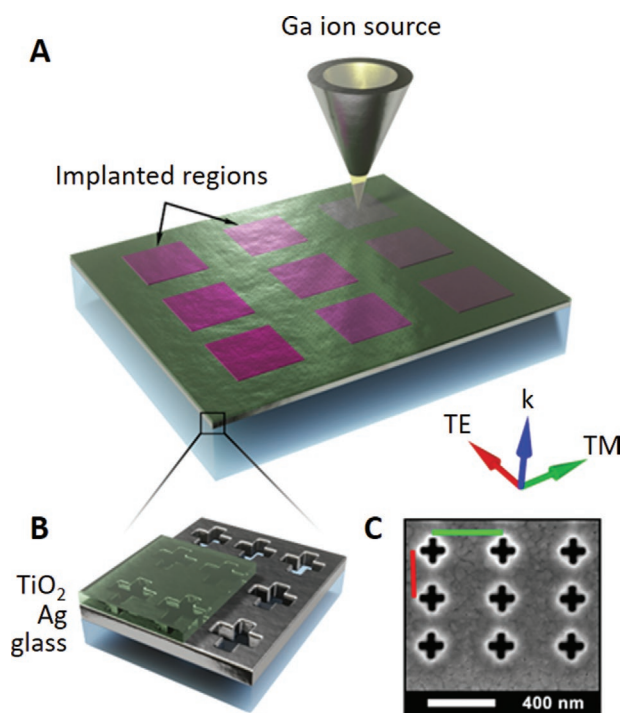


Figure 1. A) Schematic of the plasmonic device/TiO₂ being implanted with Ga³⁺ ions. The Ga ion source was raster scanned over nine separate square ($2.5 \times 2.5 \mu\text{m}$) regions with a varying implantation dose. The beam diameter, r , was 10 nm. B) The device structure consisted of an Ag film containing a periodic array of cross-shaped apertures covered by a TiO₂ thin film. C) SEM image of the plasmonic device. P_x (green line) and P_y (red line) are the array periodicities in the X and Y directions equal to 400 and 300 nm respectively.

Table 1. Ion fluence and number of ions contained within the cross-section of the ion beam. Note that the beam diameter = 10 nm, equivalent to an ion implantation area of 78.5 nm².

Implantation area	Ion fluence $\times 10^{13}$ [ions cm ⁻²]	Number of ions contained in beam [ions/beam area]
D0	0	0
D1	2	16
D2	4	32
D3	6	48
D4	12	96
D5	26	208
D6	50	400
D7	100	800
D8	200	1600
D9	400	3200

geneous distribution of ions within the implanted zone. All implanted areas were later evaluated using a spectrometer and an optical bright-field microscope. The device architecture prior to ion implantation is shown in Figure 1B; a high-resolution SEM image of the pattern is shown in Figure 1C. P_x and P_y (Figure 1C) are the periodicities, which characterize the rectangular array of the fabricated plasmonic device. They define the position of the primary resonant SPP peak, whilst the shape of the apertures determines the fine structure (peak width etc.). The values for the periodicity used in this study were chosen such that the primary resonant peak position was approximately in the middle of the visible region of the EM spectrum.

A summary of the experimental ion implantation parameters based on the known Ga ion fluences and ion beam diameter is given in Table 1. As the ion implantation dose increases it is possible to reach a level which results in the formation of a supersaturated solid solution, alloy, or compound. Whilst the Ga ion doses used are below the saturation threshold of TiO₂,^[3,4] in general, this technique is applicable to any doped thin film which constitutes a translucent matrix within the visible range. Provided the optical absorption of the ion implanted material at saturation does not prevent a measurement of the transmission plasmon resonance spectra, a study correlating the formation of local supersaturated structures to changes in the optical properties of the sample is possible.

3. Results and Discussion

In order to investigate the use of plasmonics for direct imaging of ion implantation, optical images were collected using both a bare glass substrate and the bimodal plasmonic device as a substrate for the TiO₂ thin-film. Figure 2 shows the optical images and corresponding data analysis, collected in bright-field mode, using the plasmonic device. In Figure 2A the ion implanted regions are labelled 1 to 9 with “1” indicating the lowest dose and “9” the highest. Two different incident polarization modes were used. In Figure 2A the results for the transverse electric (TE) and in Figure 2B the results for the transverse magnetic (TM) are shown.

Figure 2 shows that the chromaticity output of the ion implanted regions for both the TE and TM incident polarization only displays a relatively small variation as a function of

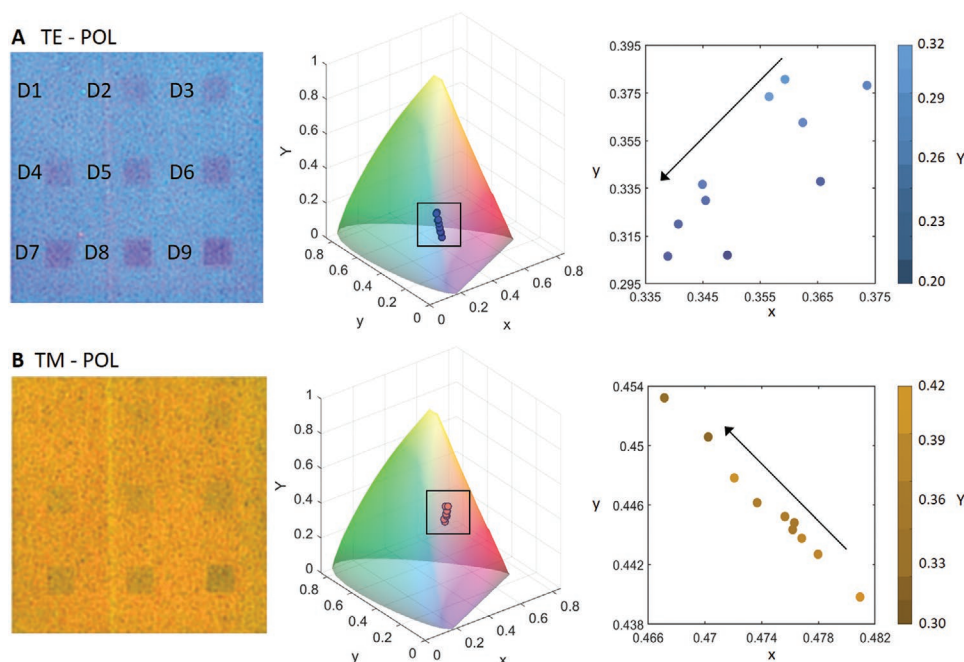


Figure 2. Bright-field optical images of the Ga-ion implanted TiO₂ thin film on the plasmonic device (left), corresponding color output plotted in the CIE 1976 xyY color space on a 3D chromaticity diagram, with x and y specifying the chromaticity and Y the luminance (middle). An enlarged plot showing the x-y chromaticity values is also presented (right). Results are shown for both A) transverse electric (TE) and B) transverse magnetic (TM) incident polarizations. The black arrows indicate the direction of increasing Ga ion implantation.

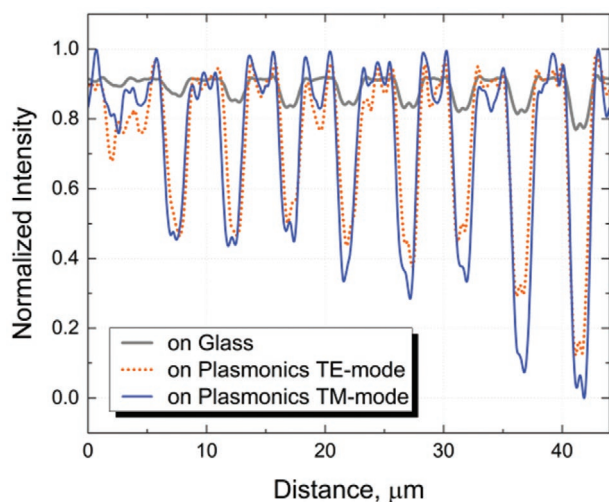


Figure 3. Line profiles taken through the middle of each of the 9 ion implanted squares. Moving from left to right on the plot the ion implantation dose decreases corresponding to squares 1 → 9. The images on the plasmonic device clearly show significant variation in the measured intensity as a function of the implantation dose consistent with the results in Figure 2.

implantation dose. The peak output for the devices is within the blue region of the spectrum for the TE mode and within the orange region of the spectrum for the TM mode. The variation in terms of the brightness is much greater than the chromaticity and can be observed directly "by eye" with around a 40% variation in the measured signal for both TM and TE modes. This was confirmed through measurement of the normalized line-profiles measured across the ion implanted areas which are shown in **Figure 3**. A dramatic increase ($\approx 450\%$) in the absorption due to ion implantation is observed when using the plasmonic device compared to the sample implantation dose measured on glass alone due to the change in the height and position of the resonant peaks when using plasmonics. The result is that by using the plasmonic device, even areas at the lower end of the scale in terms of the number of implanted ions are clearly distinguishable "by eye", whereas the signal is virtually undetectable on glass.

In contrast to the glass/TiO₂ sample where transmission is mainly characterized by classical absorption, transmission through the plasmonic/TiO₂ sample is determined via coupling of the incident light to the SPs and LSPs. This is because the TiO₂ thin film (50 nm) is thinner than the "skin depth" for this material (around 69 nm for a 600 nm incident wavelength). Therefore, changes in the dielectric constant of the TiO₂ thin film due to the presence of Ga ions are detectable as changes in the plasmonic resonant peak structure. These changes can be further enhanced and quantified by varying the polarization of the illuminating field. **Figure 3** shows the measured transmission spectra as a function of the incident wavelength for all 9 implanted areas (D1-D9) as well as the unimplanted TiO₂ thin film at both TE and TM incident polarizations (D0).

As the implantation dose increases, the transmission through the implanted areas significantly decreases (**Figures 2 and 3**), with a corresponding small change in the output color detected (**Figure 2**). The results of the analysis of the optical brightfield images are confirmed when looking at transmission spectra measured using a spectrometer (**Figure 4**). Very little variation in

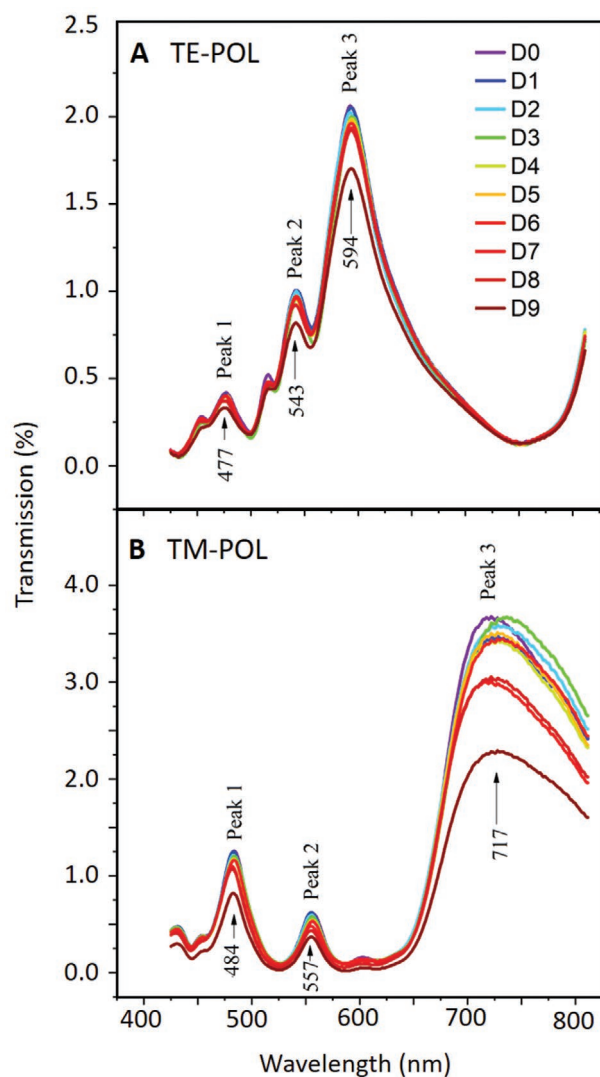


Figure 4. The transmitted intensity spectra measured as a function of wavelength for the plasmonic/TiO₂ sample taken from the unimplanted TiO₂ film (D0) and all nine Ga ion implanted areas (D1-D9) at both A) TE and B) TM incident polarizations.

the position of the primary plasmon resonance peaks is observed as a function of increasing implantation dose which is consistent with the lack of strong color contrast as a function of Ga ion density. As expected though, due to the coupling of the SPs and LSPs to the locally ion implanted TiO₂ there is a significant difference in the peak height. We observe that the difference between the implanted and unimplanted areas is greater when the sample is illuminated using the TM polarization, which is associated with the larger periodicity (400 nm) for the device compared to TE polarization. Typically, any changes in the real part of the refractive index of a material probed by a plasmonic device lead to a shift of the resonant peak position (i.e., a red shift is expected if the refractive index increases). In the case of the TiO₂ thin film, since the resonant peak position remains approximately constant, it is the changes in the height of the resonance peak, described by the imaginary part of the refractive index, which provides the greatest optical contrast.

The origin of the three plasmon resonance peaks: peak 1, peak 2, and peak 3 (P_1 , P_2 , and P_3) is associated with the different Bloch modes for the dielectric/metal SPPs, cavity LSPs, and RAs of the grating; each of which has a different mechanism of electric field propagation. The generalized dispersion relation describing the resonant peaks associated with the different Bloch modes in periodic rectangular arrays in metal films are given in the first approximation as ^[46]

$$\lambda_{\text{SPP}} \cong \frac{P}{\sqrt{i^2 + j^2}} \sqrt{\frac{\epsilon_d \epsilon_m}{\epsilon_d + \epsilon_m}} \quad (3)$$

and

$$\lambda_{\text{RA}} \cong \frac{P}{\sqrt{i^2 + j^2}} \sqrt{\epsilon_d} \quad (4)$$

where P represents the array pitch, ϵ_m and ϵ_d are the dielectric constants of the metal film (in this case TiO_2) and dielectric layer, respectively, and i and j are integers representing the diffraction orders. These dispersion relations approximate the resonance wavelength position in the transmission spectrum of the devices which can be altered by modifying the pitch of the rectangular array of nanoapertures. The dispersion relation is also strongly dependent on the dielectric constants, ϵ_m and ϵ_d . Due to the presence of interface asymmetries (glass/plasmonic and plasmonic/ TiO_2), resonant peaks arising from both interfaces are observed in the measured spectra. The resonant localized surface plasmon mode of the apertures are also present in the spectra. Stalzer et al.^[47] modelled an array of cross-shaped nanoapertures as a waveguide and calculated the TE and TM modes for different arm length-to-width ratios using the 2D scalar Helmholtz equation. Based on their model, the cut-off frequency for the main TE mode (which is situated within the spectral range studied here) is expressed as:

$$\lambda_{\text{res}} = \frac{L^2}{0.7(L-W)} \sqrt{\epsilon_d} \quad (5)$$

where L and W are the arm length and width respectively. Using this relation, the cut-off frequency for the nanoaperture array used in this study is expected to occur at around 463 nm.

It is worth noting that the peak P_1 occurs close to this cut-off at around 477 nm. Therefore, we conclude that this peak likely corresponds to one of the LSP modes of the nanoaperture array. All main SPP and RA modes occur at longer wavelengths and therefore do not interfere with this LSP mode. The P_3 peak corresponds to the SPP (1,0) Ag/ TiO_2 mode and is located at ≈ 594 and ≈ 717 nm for the TE and TM polarizations respectively. For the TE polarization mode, this peak is well defined, whereas it broadens significantly for the TM polarization due to the overlap with the SPP (1,0) Ag/glass mode. The peak P_2 occurs at 543 nm for the TE polarization and corresponds to the RA (1,0) mode, whereas the peak at 557 nm for the TM polarization is a result of the overlap of two SPP modes (1,1) Ag/ TiO_2 and (1,1) Ag/glass. There are also some smaller satellite peaks associated with higher orders of SPPs and RAs visible within the measured spectrum. From the dispersion equations the main SPP modes have the most significant impact on the transmission spectrum of the plasmonic devices. **Figure 5** shows the variation in transmission intensity for P_1 , P_2 , and P_3 as a function of Ga ion implantation dose.

Consistent with both the luminescence (Figure 2) and normalized transmission intensity (Figure 3), the plasmon resonance transmission peaks (Figure 5) clearly decrease in height (corresponding to an increase in optical absorption) as a function of Ga ion implantation. This is due to the dependence of the plasmon resonance modes on the local dielectric function of the ion implanted TiO_2 (see Equations (3) to (5)). As expected, the biggest change occurs at the TM polarization (associated with the 400 nm array periodicity) for P_3 (SPP (1,0) Ag/ TiO_2 mode). Based on the spectral data the sensitivity of the plasmonic devices to Ga ion implantation in TiO_2 is: $0.141 \pm 0.041 \times 10^{15}$ ions cm^{-2} , i.e., using the standard deviation of the TM-POL data from Figure 5B the spectral output could be used to detect differences in the ion deposition fluence of down to 4.1×10^{13} ions cm^{-2} . This is comparable, for example, to the levels of Ga ion implantation characterized in bulk diamond using ellipsometry.^[20]

In order to interpret the optical and spectral data in terms of the dielectric properties of the implanted TiO_2 regions, it is important to understand the mechanisms that induce changes in the local dielectric constant during the ion implantation process. Ion implantation is usually defined by two main

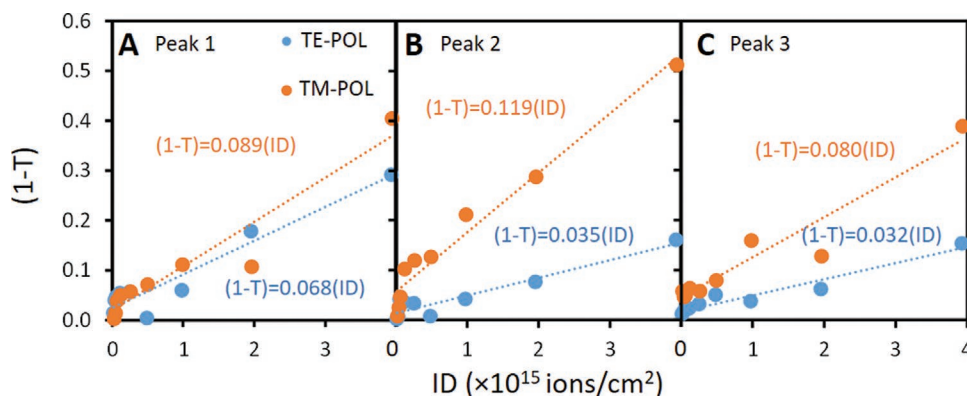


Figure 5. Relative change in the absorption ($1-T$) compared to D_0 , where T is the normalized transmission, of A) Peak 1 (P_1), B) Peak 2 (P_2), and C) Peak 3 (P_3) as a function of ion deposition fluence (ID) at both TE and TM incident polarizations.

parameters: dose (amount of implanted dopant per unit area) and implantation energy (responsible for the final depth of the dopant in the substrate). There are two primary stopping mechanisms when the ions enter the target material; the first one is the interaction of the implanted ions with the target ions (nuclear stopping), which results in a deflection of the incident ions and dislodging of the target ions. The second one is the interaction of the incident ions with the target's free and bound electrons (electronic stopping). Nuclear stopping causes physical damage and produces defects within the host lattice; electronic stopping results in vacancy-interstitials being formed. The number of displacements per target atom per unit time is described by the Kinchin-Pease relation^[48,49]

$$P(x) = \frac{0.8}{2nE_d} \left(\frac{dE}{dx} \right)_n \Phi \quad (6)$$

where Φ is the incident ion flux, n is the number density of the implanted ions, E_d is effective threshold displacement energy and $\left(\frac{dE}{dx} \right)_n$ is ion energy per unit depth. It is important to note that replacement reduces the number of vacancies that remain after the collisions by the recoil atoms. The total distance travelled by an ion before stopping is called the ion range (or ion implantation depth) and is determined by

$$R = \int_0^R dx = \frac{1}{N} \int_0^{E_0} \frac{dE}{S_n(E) + S_e(E)} \quad (7)$$

Where E_0 is the initial energy of the ion (determined by the acceleration voltage), and S_n and S_e are the nuclear and electronic stopping power respectively. In the current study, the total displacement and range of the ions in the target lattice (TiO_2) is calculated by using the stopping and range of ions in matter (SRIM) Monte-Carlo simulation software.^[48,49]

The values in Table 1 were used as input parameters for the SRIM simulations along with the ion energy in keV. Several factors play a role in determining the effect of implanted ions

on target atoms. Both the incident ion and target ion mass play an essential role in the energy transfer process. Ga ions have almost 90% of the TiO_2 ion mass and therefore every time a Ga ion hits the TiO_2 surface, it will transfer a portion of its energy to the target atoms. This means that after each collision the Ga ion has a high probability of creating a vacancy in the lattice. However, there is also a chance for the target atoms to recoil and to cause a much larger number of vacancies to form than those created by the ion collisions. **Figure 6** shows the collision plots produced from the SRIM Monte Carlo simulations of Ga ion implantation in TiO_2 .

The implantation depth of 16 keV Ga ions into TiO_2 is ≈ 34 nm (Figure 6A), which is within the detectable range of the evanescent field of the plasmons and less than the overall film thickness. Figure 6B shows the transverse implantation spread has an approximate diameter of 42 nm. If we assume that the implantation volume can be approximated as a sphere this equates to a "cluster volume" of $3 \times 10^{-17} \text{ cm}^3$. In the current experiment, each Ga ion transferred 14.7 keV (initial energy = 16 keV) to the target atoms: 9.2 keV to the Ti atoms and 5.5 keV to the O atoms. Since the energy transferred from the Ga ions to the Ti and O atoms is substantially less than their corresponding displacement energy (25 and 28 keV for Ti and O respectively) the Ga ions have a much higher probability of creating interstitials. Any energy transferred to the lattice is likely to be converted to phonons. In the current study, the monovalent Ga-doped TiO_2 film was doped using a relatively low concentration of Ga ions and thereby the induced lattice charges were compensated for by Ti and Ga interstitials (Ga^+ or Ti^{4+}).

Table 2 shows the relative contribution of impurity ions within the implanted cluster at the end of each implantation process. A super-cell lattice is considered ($x\text{Ga}[\text{TiO}_2]$) and it is assumed that x relates to the number of interstitials (Ga^+ and holes/vacancies). As a valid approximation, based on the energy loss, it is also assumed that during the implantation process only the incorporation of Ga^+ (the ion substitution in Ti^{4+}) took place with no formation of a new compound.

In our model we treat the Ga ions as spherical metal particles (with radius a) that are inclusions distributed within a

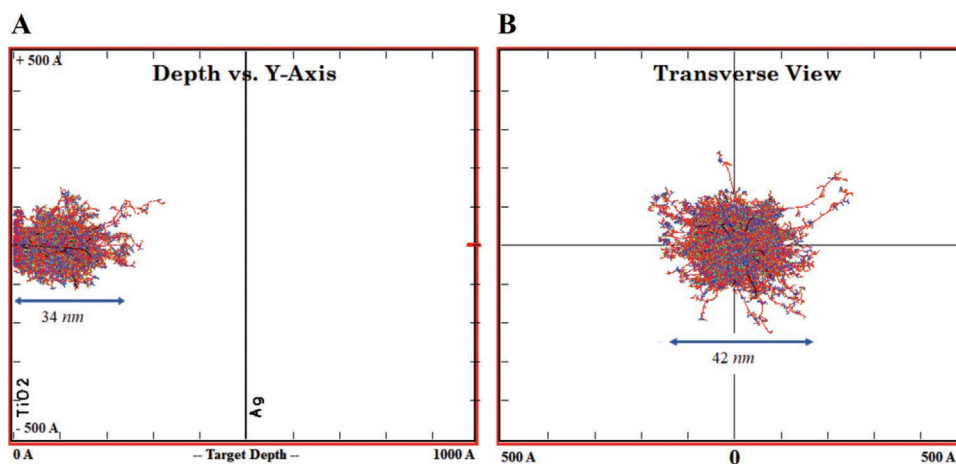


Figure 6. Still frames taken from animated collision plots generated using SRIM Monte Carlo simulations of Ga ion implantation in TiO_2 . A) The longitudinal and B) lateral projection of the ion distributions (black cascades) and recoiling atoms (blue and red cascades) and vacancies (light blue and green dots) are shown.

Table 2. TiO₂ contribution and impurity within the cluster based on SRIM calculations.

Implantation area	Number of impurity atoms $\times 10^2$ [atoms/cluster] ^{a)}	Contribution from impurity atoms within a cluster [%]
D0	0	0
D1	2	0.007
D2	4	0.013
D3	6	0.020
D4	10	0.033
D5	26	0.100
D6	50	0.167
D7	100	0.333
D8	200	0.667
D9	400	1.333

^{a)}This was determined as the product of the implanted defect density and the cluster volume which was assumed to be $3 \times 10^{-17} \text{ cm}^3$ (see description in main text).

homogeneous dielectric host (with radius h). While $0 \leq a \leq h/2$, ϵ_i and ϵ_h are taken to be the permittivity of the inclusion particle (Ga ion) and host medium (TiO₂) respectively. Typically, Lorentz molecular theory is not derived from the macroscopic form of Maxwell's equations, hence it cannot be directly applied to the calculation of macroscopic quantities such as the permittivity of a composite. However, the closely related Maxwell-Garnett mixing formula considers both the electric and magnetic dipole moments as well as the component volume fractions associated and therefore can be applied to the analysis of composites.^[50]

The specific volume per one Ga ion is: $v_{\text{Ga}} = \frac{V}{N}$, where V and the corresponding volume fraction of Ga ions is: $f = \frac{4\pi}{3} (a^3 / v_{\text{Ga}})$. Therefore, the effective permittivity, ϵ_{effGa} , of such composite is given by the Maxwell Garnet mixing formula^[51]

$$\epsilon_{\text{effGa}} = \epsilon_h \frac{1 + 2f \frac{\epsilon_i - \epsilon_h}{\epsilon_i + 2\epsilon_h}}{1 - f \frac{\epsilon_i - \epsilon_h}{\epsilon_i + 2\epsilon_h}} = \epsilon_h \frac{\epsilon_h + \frac{1+2f}{3} (\epsilon_i - \epsilon_h)}{\epsilon_h + \frac{1-f}{3} (\epsilon_i - \epsilon_h)} \quad (8)$$

here ϵ_{effGa} is the effective permittivity of Ga ion in TiO₂, (note, ϵ_{effGa} is not the usual permittivity of a Ga ion in a vacuum^[52]). The specific volume per particle is v , and the volume fraction of inclusions is f , also

$$\epsilon_h = \epsilon'_{\text{TiO}_2} + \epsilon''_{\text{TiO}_2} = (5.84 + 7.63 \times 10^{-8} i) \quad (9)$$

$$\epsilon_i = \epsilon'_{\text{Ga}} + \epsilon''_{\text{Ga}} = (-12.53 + 34.10 i) \quad (10)$$

Table 3 gives the volume fraction, the effective permittivity, and the real and imaginary part of the implanted areas at $\lambda = 578 \text{ nm}$ (this value was chosen as it lies in between P_2 for TM-POL and P_3 for TE-POL) taking into the account the relative composition presented in Table 2.

The optical constants summarized in Table 3 are shown as a function of both the relative change in the plasmon resonance peak absorption (P_2 , TM-POL) and ion deposition fluence in

Table 3. Monte-Carlo simulations of implanted TiO₂ based on the fraction of interstitials in each pattern. The volume fraction of inclusions corresponded to the SRIM simulated value.

Implantation area	Volume fraction of Ga ions $\times 10^{-3}$ (f)	Effective permittivity		Refractive index	
		ϵ'_{effGa}	$\epsilon''_{\text{effGa}}$	n_{effGa}	k_{effGa}
D0	0	5.841	7.634×10^{-8}	2.417	1.579×10^{-8}
D1	0.121	5.844	0.001	2.417	0.00023
D2	0.241	5.846	0.002	2.418	0.00045
D3	0.362	5.848	0.003	2.418	0.00067
D4	0.724	5.854	0.007	2.420	0.00135
D5	1.568	5.869	0.014	2.423	0.00292
D6	3.016	5.895	0.027	2.428	0.00562
D7	6.032	5.949	0.055	2.439	0.01127
D8	12.064	6.058	0.111	2.461	0.02261
D9	24.127	6.278	0.228	2.506	0.04552

Figure 7. Note that the linear fit in Figure 5B for TM-POL was used to convert from ID to (1-T)

As the Ga ion deposition fluence increases, the real part of the refractive index (n_{effGa}) changes from 5.841 for pure TiO₂ (D0) to 6.278 for TiO₂ Ga-doped with the highest dose (D9). Whereas the imaginary part of the refractive index (k_{effGa}) changes from 7.634×10^{-8} for pure TiO₂ to 0.228 for TiO₂ Ga-doped with the highest dose. The real part of the effective permittivity is responsible for the lateral shift in the plasmon resonance peaks ($\approx 3 \text{ nm}$ between D0 and D9 for P_3 at TM-POL). It is also primarily responsible for the small observed change in chromaticity as a function of implantation fluence (Figure 2). The change in the imaginary part of the refractive index, however, is responsible for absorption. Compared to the pristine TiO₂ the relative change in k_{effGa} is larger than that of n_{effGa} . This is reflected in both the narrow range of chromaticity values observed on the optical brightfield images as well as the relatively small plasmon resonance peak shifts compared to the overall change in peak height and optical transmission.

The relatively large change in plasmon resonance peak height as a function of implantation dose gives a simple and direct means of characterizing the ion implantation density

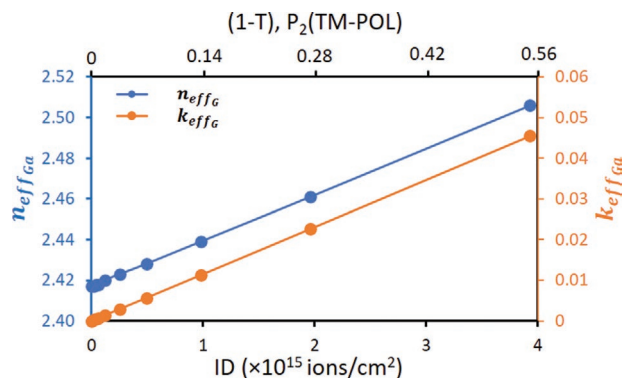


Figure 7. Optical constants n_{effGa} (blue line) and k_{effGa} (orange line) of the implanted TiO₂ plotted as a function of either (1-T) for P_2 at TM-POL (top x-axis) or as a function of the ion deposition fluence (bottom x-axis).

which could be applied to a wide range of different material systems. The analysis and equipment required to measure the optical output of bimodal plasmonic color filters is comparatively straightforward and can be carried out using a standard brightfield microscope. By building up a reference database for different implanted ions, rapid, accurate measurement of ion implantation fluence could be carried out close to the sample preparation site providing rapid feedback to the user.

4. Conclusion

Direct optical detection of implanted TiO₂ thin films was demonstrated for the first time by using biomodal color filters consisting of arrays of cross-shaped apertures in thin Ag films. The plasmon-mediated color contrast and luminosity observed in the direct imaging of these structures was correlated to the Ga ion implantation dose. Furthermore, it was demonstrated that the plasmon resonance transmission could be varied by using aperiodic arrays of apertures and a polarized light source, where the highest contrast was achieved by using the larger array pitch (TM-POL).

By employing Monte-Carlo simulations and using the Maxwell Garnett mixing formula, we were able to determine the optical constants of the Ga ion implanted TiO₂ thin films and correlate this to the implantation fluence and plasmon resonance spectra. Our simulations showed that the implantation results in Ga ions mainly residing as interstitials within the TiO₂ matrix. This produces a small change in the real part of the refractive index for the composite material but leads to a substantial change in the imaginary part of the refractive index. The result is that coupling to the SPPs and LSPs within our plasmonic color filter results in a significant and easily detectable change in the optical transmission as a function of Ga ion implantation fluence. This change in optical absorption is otherwise virtually undetectable using standard optical microscopy.

In conclusion, using direct optical imaging of the implanted material employing plasmonic nanostructures opens up new possibilities in the field of electronics where implantation is a routine technological process. Furthermore, it is possible to tune the plasmonic properties of individual biomodal plasmonic devices for the detection of a wide range of different implanted ions in a host of different materials based on their dielectric properties.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

ion implantation, materials science, metamaterials, near-field optics, plasmonics

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