Unveiling the Far Infrared – to – Ultraviolet Optical Properties of Bismuth for Applications in Plasmonics and Nanophotonics

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Abstract: Bismuth (Bi) has appealed during years a broad community of scientists due to its peculiar electronic, optical and more recently plasmonic and photocatalytic properties, which enable both the understanding of basic science phenomena and the development of a wide range of applications. In spite of this interest a comprehensive spectral analysis of the dielectric function ($\epsilon = \epsilon_1 + j\epsilon_2$) of Bi from the far infrared (IR) to the ultraviolet (UV) region is not available. So far the data have been reported in limited spectral ranges and show a wide dispersion that is especially notorious for the IR region. In this work we report ϵ for Bi in a wide spectral range from 0.05 eV to 4.7 eV (24.8 μm to 0.3 μm , far IR to UV). ϵ is extracted from spectroscopic ellipsometry measurements of excellent quality (dense and smooth) Bi films by using the transfer matrix formalism and Kramers-Kronig consistent analysis. The higher quality and accuracy of the obtained ϵ compared with the literature data is demonstrated. From the obtained ϵ it is evidenced that the optical properties of Bi in the mid wave IR-to-UV are driven *only* by interband transitions, that are responsible for a dominant absorption band peaking at about 0.8 eV. Therefore the plasmonic behaviour of Bi in the visible and UV is a consequence of these interband transitions that make ϵ_1 turn negative in this region without the need of exciting free carriers. Finally from the obtained ϵ we have simulated the optical response of Bi nanospheres in the far IR-to-near IR and it is shown that they support Mie-like resonances broadly tunable across this region.

Keywords: Bismuth, Ellipsometry, Interband transitions, Plasmonics, Mie Resonances

Bismuth (Bi) is a semi-metal with much long term interest¹⁻¹⁸ due to its many interesting properties including diamagnetism, Haas-Van de Alphen effect,¹ low thermal conductivity, high thermoelectrical coefficient, superconductivity⁵ and strongly coupled electron-plasmon “plasmaron” features¹¹ in the far infrared (IR), among others. In this context, the study and characterization of its electronic properties (in particular its band structure) has remained an active area of research from the 1960’s until today.^{2-4, 6-9, 11} Early, optical spectroscopy was used as a convenient tool to obtain information on the electronic properties of Bi crystals and films.^{2-4, 6, 7} Especially, relevant information was provided in the works of Cardona and Greenaway⁴ in 1964 and of Hunderi⁶ in 1975. These works were soon complemented by photoemission spectroscopy studies that provided rich experimental information on its energy levels.⁹ Nowadays the interest on the electronic properties of Bi has broadened,¹⁰⁻¹⁸ in relation with spintronics and quantum communications applications, especially with the discovery of spin dependent properties of Bi surfaces.

A special attention was also paid to the effect of electronic confinement in Bi nanostructures with the demonstration of a semi-metal to semiconductor transition in Bi thin films at a thickness around 30 nm.¹⁹ Later in the 2000s, the existence of quantum confinement effects in Bi nanowires and nanoparticles was discussed based on optical spectroscopy or electron energy loss spectroscopy.²⁰⁻²⁸ Especially size – dependent spectral features not observed for Bi crystals or films were evidenced in the far IR-to-mid wave IR for Bi nanowires and related with quantum confinement.²⁰⁻²⁴

Nowadays the interest on Bi nanostructures has broadened to the area of plasmonics that at present is one of the most active fields of material science.^{29,30} The growth of this field has been impulsed by the capability of noble metal nanostructures to strongly absorb, scatter, or confine light at their localized surface plasmon resonances that enable the construction of useful devices impacting in different technological areas. It has been shown that such plasmonic properties are not restricted to noble metals and they can also be achieved with other elemental metals,³¹ metallic compounds,³¹⁻³⁴ heavily doped group IV semiconductors³² or transparent conductive oxides.³² In all these cases, they are enabled by the free carrier – induced negative values of the real part ϵ_1 of the dielectric function of the material ($\epsilon = \epsilon_1 + j\epsilon_2$).³⁵ In this context recently it has been shown that Bi nanostructures show plasmonic properties in the visible – UV and in the far IR. Specifically, works performed by our group have demonstrated localized surface

plasmon-like resonances for Bi nanostructures in the visible – UV region.³⁶ These resonances are interesting for the design of tunable metamaterial filters for integrated photonic devices,³⁷⁻³⁸ and in addition they have attracted the attention of other groups interested in surface enhanced spectroscopy³⁹ and plasmonic-enhanced photocatalysis.⁴⁰⁻⁴¹ Other groups have been interested in Bi microstructures in relation with their plasmonic properties in the far IR.⁴² Moreover, it has been proposed that the plasmonic properties of Bi in the visible - UV and far IR are induced by different elemental mechanisms: the excitation of interband transitions and the excitation of free carriers, respectively.^{43,44} The former case is of particular interest, as it opens the way to the achievement of *visible – UV plasmonic properties without free carriers* that could be tunable through the tailoring of band structure and the occupation of electronic states.^{44, 45} However to be certain that such an “*interband plasmonic*” mechanism takes place, it is mandatory to know at least the “bulk” dielectric function of Bi with precision in a broad spectral range from the far IR to the UV. The knowledge of such a dielectric function is also essential as a reference for the assesment of quantum size effects in Bi nanostructures. However as we will see, there is no work reporting accurately this dielectric function in the whole range from the far IR to the UV. Furthermore the values obtained from the different reports are not consistent especially in the IR region in which it seems that the optical properties of Bi nanostructures largely remain to be explored.

Given the long and continued interest in the electronic and optical properties of Bi for different applications up to the present days, there are many studies that have reported the optical properties and the dielectric function of Bi samples. They have been determined by different spectroscopic techniques, in each case in a different and limited spectral range.^{6,11,36,44,46-53} The samples were crystals or films, prepared by different methods and in most cases scarce information about the nano/micro-structure and surface morphology of the samples was provided. Therefore, it is questionable whether the reported dielectric functions are intrinsic to Bi or include artifacts related with the specific structural features of the samples, such as porosity or surface roughness. In sum, although there are partial reports on the optical properties of Bi, there is not a consistent and reliable report of its dielectric function in the spectral range covering from the far IR to the UV.

For the accurate determination of the dielectric function of Bi, it is primordial to perform the optical characterization of a pure Bi material presenting a high density and low surface roughness. Therefore we have prepared high optical quality, dense and smooth Bi films, verified upon characterization of their nanostructure and surface morphology. The optical properties of these films have been characterized from 0.05 eV to 4.7 eV (24.8 μm to 0.3 μm) by spectroscopic ellipsometry. By a careful analysis of the measured spectra involving a realistic model, the Kramers-Kronig consistent dielectric function of Bi has been obtained thus providing the first coherent and consistent dataset for this material from the far IR to the UV. In the **Results section**, we report the structure, ellipsometric response of the films, and the obtained dielectric function that we compare with those reported previously in the literature that show a broad dispersion especially in the IR region. We demonstrate the higher quality of our dielectric function compared to most of these previous reports. In the **Discussion and Applications section**, we relate this dielectric function with the electronic structure of Bi. We use it to ascertain the “interband plasmonic” behaviour of Bi in the visible - UV, and to explore for the first time the optical response of Bi nanospheres in the far IR-to-near IR region.

Results

Fabrication and Characterization

Bi films were fabricated by pulsed laser deposition in high vacuum on p-type single side polished silicon (Si) substrates held at room temperature. The back side of the substrates was further roughened mechanically prior to deposition. The fabrication procedure and deposition conditions are detailed elsewhere.⁵⁴ Rutherford backscattering spectroscopy (RBS) experiments were performed on the obtained samples. They do not show the presence of impurities, and yield a Bi areal density of $218.6 \times 10^{15} \text{ atoms/cm}^2$. Assuming that the films have the same density as pure bulk Bi ($2.8 \times 10^{22} \text{ atoms/cm}^3$), one derives a nominal film thickness $t_{\text{bismuth nominal - RBS}} = 78 \pm 2 \text{ nm}$. The nanostructure of the films was studied by scanning electron microscopy (SEM) with an Hitachi SU 8000 FE-SEM. The topography of the films was characterized by atomic force microscopy (AFM). A Multimode 8 AFM with NanoScope V controller (Bruker) was used under

tapping mode with NSG-30 probes (NT-MDT). Analysis was performed with the NanoScope Analysis 1.50 software (Bruker).

Spectroscopic ellipsometry characterization was carried out from the far IR (0.05 eV) to the near UV (4.7 eV) using two different setups: for the far IR-to-near IR (0.05 eV to 0.7 eV) an IR VASE ellipsometer (Polarizer-Sample-Rotating Compensator-Analyzer configuration, Woollam Co. Inc.), and for the near IR-to-near UV (0.75 eV to 4.7 eV) a VASE ellipsometer (Polarizer-Retarder-Sample-Rotating Analyzer configuration, Woollam Co. Inc.). The data were acquired at angles of incidence of 30°, 40°, 50°, 60° and 70°. At an angle of incidence of 70°, the illuminated area on the sample had an elliptic shape with size of about 10 x 50 mm for the IR VASE and of about 2 x 6 mm for the VASE. The obtained data were analyzed using the WVASE32 software (Woollam Co. Inc.) that allows multiangle fitting of the spectra using the transfer matrix (Abelés) formalism. Finally, a realistic model including the substrate, the film and a surface roughness layer has been built to account for the real structure of the samples. Variable angle spectroscopic ellipsometry⁵⁵⁻⁵⁶ with realistic sample modeling has been recently used to provide the dielectric function of gold (Au) and silver (Ag) with improved accuracy compared with earlier works involving other spectroscopic methods and simpler data analysis procedures.⁵⁷⁻⁵⁸

Structure

Figure 1a shows plan-view and tilted (inset) images obtained by SEM. The tilted image shows a dense film with low surface roughness. The plane-view image suggests the presence of surface nanostructures with lateral dimensions around 100 nm. A refined determination of the topography of the film is provided by the AFM data (image and profile) shown in figure 1b, confirming that there are surface nanostructures with lateral dimensions around 100 nm, and it can be determined that their height is lower than 10 nm. From the analysis of the RBS, SEM and AFM data, we conclude that the films can be described as shown in figure 1c: they consist of a dense, sub-100 nm thick Bi layer deposited on the flat Si substrate. This layer supports a thin nanostructured Bi surface roughness layer, in which the height of the nanostructures is of a few nm.

Figure 1: (a) Tilted view and plane-view SEM images of a Bi thin film with a nominal thickness of 78 nm deposited on a Si substrate. (b) AFM image and profile of the thin film. (c) Schematic representation of the sample structure.

Optical Response

Figure 2a (red dots) shows the measured ellipsometric (Ψ and Δ) spectra obtained with the IR setup (IR VASE, left panels) and with the near IR-to-near UV setup (VASE, right panels). There is an excellent spectral continuity between the data obtained with the two different setups. These spectra show low noise in the full photon energy range. The depolarization values (not shown) are very low, overcoming 10% only with the IR VASE setup at an angle of incidence of 70° for photon energies between 0.6 and 0.7 eV. The high quality of the measurements is in agreement with the low surface roughness and high homogeneity of the films.

The Ψ and Δ spectra were fitted using the following model (shown in figure 2b) that takes into account the real structure of the sample as determined by SEM and AFM measurements: semi-infinite Si substrate/dense Bi layer/nanostructured roughness layer. The Si substrate was described by dielectric functions taken from the Woollam database (Si_ir.mat in the far IR-to-near IR, Si.mat in the near IR-to-near UV). The dense Bi layer was described by a Generalized Oscillator model consisting of the sum of 9 Lorentz oscillators plus a Drude function, this approach enables a full Kramers-Kronig consistency for its total dielectric function $\epsilon = \epsilon_1 + j\epsilon_2$. The nanostructured roughness layer was described by a standard EMA Bruggeman model mixing the dielectric functions of the underlying dense Bi layer and of vacuum with a 50%/50% proportion. The free parameters of the fit were the position, amplitude and width of the oscillators, the parameters of the Drude function, and the thicknesses t_{bismuth} and $t_{\text{roughness}}$ of the dense Bi and nanostructured roughness layers. The best fit Ψ and Δ spectra (figure 2a, black curves) are in excellent agreement with the measured spectra at all the angles of incidence. The best fit thicknesses were $t_{\text{bismuth}} = 73.3$ nm and $t_{\text{roughness}} = 8.3$ nm, respectively. The $t_{\text{roughness}}$ value is in very good agreement with the AFM data that yielded a height below 10 nm for the surface nanostructures as explained above. Moreover, these data allow to calculate the total nominal thickness of Bi in the stack using the expression $t_{\text{bismuth nominal - ellipsometry}} = t_{\text{bismuth}} + 50\% t_{\text{roughness}}$. This calculation yields a value of 77.5 nm, i.e, very close to that provided by RBS, $t_{\text{bismuth nominal - RBS}} = 78$ nm. This excellent agreement suggests that the dense Bi layer has the same density as pure bulk Bi. This result, together with the low measured roughness, point toward the excellent structural and optical quality of the fabricated films. This makes them fully suitable for the accurate determination of *the dielectric function of Bi*, which is thus given by *the dielectric function $\epsilon = \epsilon_1 + j\epsilon_2$ of the dense Bi layer*.

(a)

(b)

Figure 2: (a) Experimental (red dots) ellipsometric spectra (Ψ and Δ) for a Bi film with a nominal thickness of 78 nm deposited on a Si substrate, and the corresponding best fit spectra (black curves). (b) Model used for fitting the experimental spectra.

Figure 3 shows the best fit spectrum of this dielectric function ϵ , in the 0.05 eV to 4.7 eV range (black lines). The corresponding parameters for the Drude function and Lorents oscillators are given in **section S1**. Note that a very similar dielectric function is obtained for thicker Bi films (thickness > 100 nm), as described in **section S2**, showing the invariance of the dielectric function of Bi as a function of thickness. This also means that the obtained dielectric function ϵ does not include any artifact due to correlation between the oscillator parameters and the thickness, thus further proving the consistency of our analysis.

Figure 3: Best fit dielectric function $\epsilon = \epsilon_1 + j\epsilon_2$ of the dense Bi layer (black lines), together with selected dielectric functions attributed to Bi found in the literature: Hunderi1975 (100 nm film),⁶ Toudert2012 (120 nm film),³⁶ Hodgson1954 (crystal),⁴⁶ Lenham1965 (crystal, along the basal plane and along the optical axis),⁵¹ Khalilzadeh2015 (6 μm e-beam evaporated and 12 μm thermally evaporated film),⁵² Tediosi2007 (crystal),¹¹ Harris1963 (170 nm film).⁴⁸ The different spectral regions are defined as follows: UV – above 3.3 eV; visible – 3.3 eV to 1.7 eV; near IR – 1.7 eV to 0.89 eV; short wave IR – 0.89 eV to 0.41 eV; mid wave IR – 0.15 eV to 0.41 eV; long wave IR – 0.08 eV to 0.15 eV; far IR – 0.01 eV to 0.08 eV.

The most relevant features that we observe are: i) *negative ϵ_1* values above 0.8 eV (i.e. especially in the visible - UV), ii) a *strong absorption band* in the ϵ_2 spectrum peaking in the short wave IR around 0.8 eV (with values higher than 100!), iii) *high positive ϵ_1* values (up to more than 100!) between 0.1 eV and 0.6 eV (i.e. in the long wave IR-to-short wave IR), iv) a *decrease in ϵ_1* and an *increase in ϵ_2* when photon energy decreases below 0.1 eV to the far IR. These features will be discussed in relation with the electronic band structure of Bi in the **Discussion and Applications** section. Note that we have chosen a logarithmic scale for the energy axis of figure 3 to facilitate the visualization of the previously cited spectral features.

For the sake of comparison with earlier works, figure 3 also gathers relevant dielectric functions of Bi samples taken from the literature. Note that they were obtained by different spectroscopic techniques including ellipsometry and reflectance measurements, and the analysis of the data in some cases did not include a Kramers-Kronig consistent approach. In the following we review some of the more relevant data.

Lenham et al.⁵¹ reported the dielectric functions of surface polished Bi monocrystals in their bisectrix – binary axis plane (hereafter called “basal plane”) and along their trigonal axis (perpendicular to the basal plane), from the long wave IR to the UV. The analysis revealed uniaxial anisotropy in the mid wave IR region, in relation with the structural anisotropy of the rhomboedral elementary cell of Bi. The optical axis of Bi is oriented along its trigonal axis. Thus the extraordinary (ordinary) dielectric function of Bi is measured for the electric field along this axis (in the basal plane). Tediosi et al.¹¹ studied the ordinary optical properties of cleaved Bi monocrystals by performing reflectance measurements with a standard IR spectrometer and with the incident electromagnetic field in the basal plane of the crystal. They did a Kramers-Kronig consistent analysis taking into account ellipsometric data measured in the 0.7 to 4.5 eV range, and reported only the imaginary part of the measured ϵ at far IR photon energies (less than 0.1 eV).

De Sande et al.⁵⁰ reported the dielectric function of DC magnetron sputtered and pulsed laser deposited Bi films in the visible and UV (1.55 eV to 4 eV). They showed that a consistent determination of the dielectric constant of the films could be obtained only for those deposited by pulsed laser deposition, whereas for the DC sputtered films the results vary with the film thickness. The film quality was assessed by a combination of SEM and TEM analysis and showed that the pulsed laser deposited films were dense and smooth, whereas the DC magnetron sputtered films were porous and rough. No information of the procedure for data analysis is provided, however most likely direct inversion from the ellipsometric measurements was used. Toudert et al.³⁶ reported the dielectric function of similar pulsed laser deposited films in a broader region, ranging from the short wave IR to the UV (0.75 eV to 4 eV). The analysis of the data in this case included the modeling of the dielectric function with the sum of a Drude function and Kramers-Kronig consistent Lorentz oscillators. The data from these two reports overlap with those of the present work in the visible and UV regions (for the sake of clarity, we have thus not plotted in figure 3 the data from De Sande et al.). Note that the

pulsed laser deposited Bi films are reported to show a preferential orientation with their trigonal axis perpendicular to the substrate.⁵⁹ This orientation has been checked in the present work by x-ray diffraction, as explained in **section S3**. Therefore, the optical axis of these films is oriented perpendicularly to the substrate. In these conditions, spectroscopic ellipsometry is weakly sensitive to the extraordinary component of the dielectric tensor.⁶⁰ As a consequence, the data shown by De Sande et al.,⁵⁰ Toudert et al.,³⁶ and in the present work corresponds most likely to the ordinary dielectric function of Bi, i.e. in its basal plane.

Hodgson (mid wave IR-to-visible),⁴⁶ Hunderi (short wave IR-to-UV),⁶ Harris et al. (far IR),⁴⁸ and Khalilzadeh-Rezaie et al. (far IR-to-short wave IR)⁵² reported the dielectric function of polycrystalline Bi films grown by evaporation. Among these four reports, and according to the information provided on the films morphology, the best film quality seems to have been achieved in Hunderi's work, in which the substrates were kept at low temperature during the growth.⁶ By such means, the formation of surface roughness and/or porosity was likely avoided. This was not the case in the work of Khalilzadeh-Rezaie,⁵² where the substrates were not cooled and the deposition was performed in several steps. This induced the formation of a marked surface roughness with clear columnar-like structures, the compacity and lateral dimensions of which depend on the type of evaporation process: well separated 100 nm structures for thermal evaporation and more densely packed 500 nm structures for e-beam evaporation.

An important result that has to be underlined from figure 3 deals with the dispersion of the data obtained from the different works in the IR. This dispersion is especially apparent from the ϵ_1 spectra. The spectrum obtained for our pulsed laser deposited Bi films and that given by Hunderi⁶ show the highest ϵ_1 values among all the literature, above 100 at photon energies between 0.6 and 0.8 eV. It is worth noting that Hunderi's spectrum nicely overlaps with the data in this work in the short wave IR-to-UV. This correlates with the excellent quality (low roughness and low porosity) of the films grown by pulsed laser deposition and those evaporated onto low temperature substrates. Lower maximum ϵ_1 values (70 between 0.2 eV and 0.7 eV) have been obtained by Lenham et al.⁵¹ Even lower maximum values have been reported by Khalilzadeh-Rezaie,⁵² with a ϵ_1 of 50 at 0.09 eV for e-beam evaporation and of 25 at 0.07 eV for thermal evaporation. We show below that these lower maximum values and the fact that

they appear at lower energies than in the case of our pulsed laser deposited films is a consequence of not taking into account the higher surface roughness of crystals or evaporated films in the analysis of ellipsometry data.

In the works of Hodgson,⁴⁶ Lenham et al.⁵¹ and Khaliladzeh-Rezaie et al.,⁵² the Bi material was analyzed as a semi-infinite medium, i.e. its dielectric function was directly inverted from ellipsometry measurements using Fresnel equations regardless of the presence of surface roughness and possibly of porosity. This direct inversion yields the so-called “pseudo-dielectric function” $\langle \epsilon \rangle$ of the material. In figure 4, we show the simulated real part $\langle \epsilon_1 \rangle$ of the pseudo dielectric function calculated for a semi-infinite Bi medium without and with a surface roughness layer, for different layer thicknesses (5 nm, 20 nm, 50 nm). In the calculations, the dielectric function of Bi was taken from figure 3 (“this work”, black line), and the dielectric function of the surface roughness layer was calculated using a standard EMA Bruggeman model (50% Bi – 50% vacuum).

Figure 4: Simulations of the real part of the pseudo-dielectric function $\langle \epsilon \rangle$ of a semi-infinite Bi medium (bulk Bi, dielectric function of Bi obtained from figure 3), and of a semi-infinite Bi material with a surface roughness layer of given thickness (5 nm, 20 nm, 50 nm). The roughness layer was modeled with a standard EMA Bruggeman model (mixing the dielectric functions of Bi and vacuum with a 50%/50% volume proportion).

Upon increasing the thickness of the roughness layer, the maximum of $\langle \epsilon_1 \rangle$ decreases and shifts toward lower photon energies. For a 50 nm thickness, a maximum of 60 is reached for $\langle \epsilon_1 \rangle$ at a photon energy of 0.1 eV, i.e. very comparable to Khalilzadeh-Rezaie results for the e-beam evaporated Bi films (figure 3). Simulations also show (not plotted here) further reductions in the $\langle \epsilon_1 \rangle$ values upon introducing porosity in the underlying semi-infinite Bi medium.

These simulations, although very simple and qualitative, suggest that the dielectric functions reported by Khalilzadeh-Rezaie,⁵² and to a lesser extent, by Lenham et al.⁵¹ and Hodgson⁴⁶ are not intrinsic to Bi but include artifacts related with the direct inversion of ellipsometry data on a material presenting surface roughness and/or porosity. In summary, we propose that the dielectric function measured in this work shows the highest quality among all the literature. It overlaps with the best previously reported data in the short wave IR-to-UV (Hunderi⁶) and has no equivalent in the far IR-to-short wave IR region.

Discussion: Towards the Understanding of the Optical Properties of Bismuth Nanostructures

Analysis of the Dielectric Function of Bulk Bismuth

As mentioned in the introduction, the optical properties of Bi nanostructures remain to be explored and understood. At such aim, it is first necessary to analyze and understand the dielectric function of bulk Bi. Therefore, we discuss here the relation between the main spectral features of the dielectric function ϵ determined in this work (shown in figure 3, black lines) with the electronic band structure of Bi. As already remarked in the **Results section**, an important feature of the ϵ_2 spectrum is a strong absorption band peaking around 0.8 eV. This strong absorption band was also reported in the work of Hunderi⁶ and was associated to interband transitions with onset near the Γ point, $\Gamma_6^+ - \Gamma_6^-$ and $\Gamma_{45}^+ - \Gamma_6^-$. Later in their calculations of the band structure Liu and Allen⁸ found that this range of energy is also associated to interband transitions near the T point $T_6^- - T_{45}$. Therefore at least three interband transitions are contributing to the observed strong absorption. Negative ϵ_1 values are observed at higher photon energies than this strong sharp absorption band, i.e. in the visible and UV. This behaviour is typical of Kramers-

Kronig relations and the causality principle which imply a decrease in ϵ_1 at the high energy side of spectrally localized optical transitions. When these optical transitions have a sufficiently high oscillator strength, ϵ_1 can even turn negative.

Another important feature of the obtained dielectric function is the decrease in ϵ_1 and increase in ϵ_2 upon decreasing photon energy below 0.1 eV. This feature is linked with the excitation of free carriers and the fact that it starts to be relevant in the far IR only suggests that the free carrier density/relative effective mass ratio is very low. This is consistent with the electronic structure of Bi that consists of three s and two p bands separated by several eV. However the p bands cross the Fermi level at the T and L points of the Brillouin zone creating hole pockets at the T points and electron pockets at the L points. These pockets are very shallow (tenths of meV) and this in turn leads to a very low carrier density of around 10^{17} cm^{-3} - 10^{18} cm^{-3} and small relative effective masses of the carriers of 0.01 to 0.1.^{7,48}

Ultraviolet - Visible Optical Properties of Bismuth Nanostructures: Interband Plasmonics and Photocatalysis

The previous discussion supports the fact that the negative ϵ_1 values in the visible and UV and thus the reported plasmonic properties of Bi nanostructures in this region are induced with no contribution of free carriers, and are instead due to the excitation of interband transitions with high oscillator strength. This interpretation appeals to a new paradigm in photonics that is the possibility of achieving “*interband plasmonic*” *properties in the visible and UV without free carriers.*⁴⁴⁻⁴⁵

For the sake of completeness we now provide a quantitative validation of this result (that was discussed in ref. 44 on the basis of literature data) by showing in figure 5 the total contribution of the Lorentz oscillators (accounting for interband transitions, violet line – All Oscillators) and of the Drude function (accounting for free carriers, green line – Drude) to the dielectric function of Bi determined in this work (dashed black line). Note that the Drude parameters (see **section S1**), in particular the free carrier density of $1.85 \cdot 10^{18} \text{ cm}^{-3}$ and the relative effective mass of 0.01, are in qualitative agreement with other reports on the electronic properties of Bi.^{7,48} As expected, in relation with the very low free carrier density to relative effective mass ratio, in the figure the Drude function

is negligible in the visible-UV region where the dielectric function of Bi is therefore totally ruled by interband transitions.

Figure 5: Contribution of interband transitions (modeled as a sum of Lorentz oscillators, “All Oscillators”, violet lines) and free carriers (modeled by a Drude function, “Drude”, green lines) to the real ϵ_1 and imaginary ϵ_2 parts of the dielectric function of Bi determined in this work (“Drude + All Oscillators”, black dashed lines). The imaginary part of the individual Lorentz oscillators is also shown (“Individual Oscillators”, violet dashed lines).

Note that this result is based on the analysis of the ordinary dielectric function of Bi (in the basal plane) which is the only one we have access to in this work. To ascertain the “interband plasmonic” behaviour of Bi for *any orientation* of the electric field of the incident light, a knowledge of the extraordinary dielectric function of Bi in the full far IR-to-UV would be required. This information is not available in the literature, and could be achieved by performing broadband generalized ellipsometry on cleaved monocrystals with a suitable orientation. Nevertheless, some key information can already be found in a few reports. Lenham et al.⁵¹ observed no contribution of free carriers to both the ordinary and extraordinary dielectric functions of Bi monocrystals

from the long wave IR to the UV. Although they reported a significant anisotropy in the mid IR, it is most likely due to the polarization - dependence of interband contributions. This trend agrees with the results of Gerlach et al.⁶¹, who reported the ordinary and extraordinary dielectric functions of Bi monocrystals in the far IR and showed that the free carrier contribution start to be sizeable only at photon energies below 50 meV regardless the orientation of the electric field of the incident light. As a conclusion, it seems that the plasmonic properties of Bi in the UV-visible are driven only by interband transitions (without free carrier contribution) whatever the orientation of the electric field of the incident light.

Therefore, the optical resonances reported in the UV-visible for Bi nanostructures³⁶⁻³⁸ may stand on the excitation of interband transitions only, with no contribution of free carriers. To be exact, they should thus be named “*interband polaritonic resonances*”. Note, however, that this terminology is not employed in the literature for similar phenomenae that remain named “plasmons”, such as the interband π -plasmon of graphene,⁶² or the plasmons reported by electron energy loss spectroscopy on semiconductors such as Si or Ge. These results are particularly relevant in the context of the numerous works reported recently that demonstrate the excellent photocatalytic properties of Bi nanostructures.⁶³⁻⁷³ In the photon energy region of the interband polaritonic resonance (determined by the geometry of the Bi nanostructure), the incident light generates electron-hole pairs with a much higher density than it would in bulk Bi. These photogenerated carriers can be used to activate chemical reactions at the surface of the Bi nanostructures, in a similar way as hot electrons in traditional plasmonic nanostructures.⁷⁴ Since the interband polaritonic resonances can be tuned in the whole UV-visible range, the full solar spectrum can potentially be exploited for the photoactivation of chemical reactions at the surface of Bi nanostructures. Let us finally remark that the photoactivation of chemical reactions through the excitation of interband transitions in nanostructures is not specific to Bi: it has been reported in transition metals such as Pd, Pt or Rh.⁷⁵ Indeed, the plasmonic behaviour of these metals in the UV-visible is also mainly driven by interband transitions.

Infrared Optical Properties of Bismuth Nanostructures: Mie Resonances and Electronic Confinement Effects on the Band Structure of Bismuth

In view of the broad dispersion of data found in the literature for the “bulk” dielectric function of Bi in the IR, it becomes clear that the optical properties of Bi were not accurately known so far in this region. This absence of a well-defined “bulk” reference has limited the understanding of the effects driving the IR optical properties of Bi nanostructures. Surprisingly, the IR optical properties of Bi nanospheres have not been reported so far. In order to start filling this gap in the knowledge, we show here optical extinction efficiency (Q_{ext}) spectra calculated with the Mie theory (using the MiePlot software⁶²) for a Bi nanosphere as a function of its diameter D and of the nature of the surrounding medium. The dielectric function of Bi determined in this work (black lines in figure 3) was used for the nanosphere. D was varied from 100 nm to 2 μm . Figure 6 shows the Q_{ext} spectra obtained for the different values of D for a nanosphere embedded in a transparent surrounding medium with a dielectric constant ϵ_m of 1 (e.g. vacuum). Interestingly, one resonance can be seen at approximately 0.5 eV for a diameter of 200 nm. Upon increasing D , it shifts towards lower energy while its amplitude increases and then decreases. Upon varying D up to 2 μm the spectral position of the resonance can be tuned down to a photon energy of 0.08 eV that is to say over the whole far IR-to-short wave IR region. This observed resonance can be put in relation with the very high ϵ_1 values (around 100) and the non-zero but lower ϵ_2 values (between 20 and 40) in this region. Probably, these values of ϵ_1 and ϵ_2 allow the excitation of IR (lossy) Mie-like resonances in Bi nanospheres, in a similar way as Mie resonances are excited in the visible in Si nanospheres.⁶² When the Bi nanosphere is embedded in a medium with a higher dielectric constant, these resonances tend to disappear (see **section S4**), in a similar way to the trends observed for the Mie resonances of Si nanospheres. In these conditions, the Q_{ext} spectrum shows only a “bandgap-like” onset that shifts toward higher energies upon decreasing D . Moreover, even for relatively large D values there is no trace of the strong interband absorption peak at 0.8 eV that is seen in the ϵ_2 spectrum of bulk Bi or in the transmission spectrum of a thin slab with the dielectric function of bulk Bi (see **section S5**).

These results have important implications for the understanding of confinement effects on the band structure of Bi. They show that, even without considering any deviation

from the bulk value for their dielectric function, Bi nanostructures can present very different extinction spectra when compared with Bi thin films. This is just a consequence of the fulfilment Maxwell equations and boundary conditions for the electromagnetic field. In order to properly identify changes in the band structure of Bi due to confinement, it is therefore required to “correct” the experimental data (usually, extinction spectra) of Bi nanostructures from these classical electromagnetic effects to extract the dielectric function of the confined material that will be compared with that of bulk Bi. Electronic confinement effects on the band structure of Bi have been sought so far mainly in Bi nanowires.²⁰⁻²⁴ The “correction” from classical electromagnetic effects was done in refs 21-24 on the far IR-to-mid IR transmittance spectra of arrays of Bi nanowires. This allowed to evidence absorption features in the far IR (near 0.1 eV) that were attributed to intersubband transitions occurring as a result of electronic confinement in the nanowires. In ref 20, the extinction of single Bi nanowires with different diameters (from 30 nm to 400 nm) was measured from the long wave IR to the short wave IR. No trace of the strong interband absorption peak at 0.8 eV was reported, and a “bandgap-like” onset of absorption shifting toward higher energies as the diameter decreases was seen. These trends were attributed to changes in the band structure of Bi due to electronic confinement, however without performing any “correction” from classical electromagnetic effects nor any comparison with measurements on bulk Bi. At the light of the simulations shown on figure 6 and in **section S4**, it is questionable whether the trends reported in this reference are due to changes in the band structure of Bi or to classical electromagnetic effects.

In sum, it seems that much remains to be done for the understanding of the optical properties of Bi nanostructures (especially in the IR region) and of their band structure. To succeed in the quest for that understanding it will be necessary to fabricate a broad variety of Bi nanostructures with a controlled size and shape, perform accurate optical measurements possibly on single nanostructures, and extract their dielectric function using adequate mathematical approaches. As a first step, it could be already interesting to simulate by numerical methods the measurable IR optical properties of nanostructures such as nanowires or nanorods (for instance their extinction spectra) using the dielectric function of bulk Bi obtained in this work, and compare the results with measurements. Differences between simulated and measured data will reflect

changes in the dielectric function and band structure of Bi with respect to the bulk. This task is however beyond the scope of this paper.

Figure 6: Extinction efficiency of a Bi nanosphere calculated using the Mie theory for different diameters D . The dielectric function of the nanosphere was that of Bi determined in our work (figure 3, thick black lines) The nanosphere is embedded in a transparent medium with a dielectric constant $\epsilon_m = 1$.

Bismuth: Analogy with Silicon

These findings suggest that a broad variety of resonances with different physical origins can be achieved in Bi nanostructures: “interband plasmonic” resonances in the visible and UV, Mie-like resonances in the far IR-to-short wave IR, “free-carrier” plasmonic resonances in the far IR. To some extent, this behaviour can be compared to that of Si that shows strong interband transitions in the deep UV: thus Si nanostructures can support “interband plasmonic” resonances in the vacuum UV and Mie resonances in the near IR and visible. Moreover, “free-carrier” plasmonic resonances can be achieved in Si nanostructures and tuned from the far IR-to-mid wave IR through doping.³² Therefore, this analogy with Si can be useful for the understanding and tuning of the optical properties of Bi nanostructures.

Conclusions

We have fabricated reference Bi films, with high density and a smooth surface and measured their optical properties from the far IR to the UV by spectroscopic ellipsometry. The spectroscopic data have been analyzed using a realistic multilayer model that allowed extracting accurately the Kramers-Kronig consistent dielectric function $\varepsilon = \varepsilon_1 + j\varepsilon_2$ of Bi. The obtained dielectric function shows a strong multicomponent absorption band in the short wave IR that is attributed to several interband transitions. It is the first time that this multicomponent band is fully resolved and reported. We have been able to observe it unambiguously due to the excellent optical quality of the films and the use of an adequate model for data analysis. This allows us to report for the first time a high quality, artifact-free (free of porosity-induced or surface roughness-induced effects) “bulk” dielectric function of Bi from the far IR to the UV that will be useful for understanding and modeling the optical response of Bi nanostructures for fundamental and applied purposes.

Especially we show that the strong short wave IR absorption band induces negative ε_1 values in the visible and UV that are *fully* responsible for the plasmonic properties of Bi in this region. Indeed, as expected from the band structure of Bi it is shown that free carriers cannot be excited optically in the visible and UV, the free-carrier contribution to ε_1 becoming sizeable only in the far IR. This finding ascertains the “interband plasmonic” behaviour of Bi in the visible and UV. Moreover, we predict that Bi nanostructures shall display Mie-like resonances tunable in the far IR-to-short wave IR upon control of the nanostructure size. These properties are not unique to Bi and opens the way to switchable nanophotonics through the tuning of the electronic structure of the material.^{44,45,63}

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Supporting Information Available

Parameters of the Drude function and Lorentz Oscillators (S1). Analysis of thicker films (S2). This material is available free of charge *via* the Internet at <http://pubs.acs.org>.

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