POLITECNICO MILANO 1863

SCUOLA DI INGEGNERIA INDUSTRIALE E DELL'INFORMAZIONE

EXECUTIVE SUMMARY OF THE THESIS

Development of alternative plasmonic Ta:TiO_2/TiN multilayers as a platform for novel hyperbolic metamaterials

TESI MAGISTRALE IN MATERIALS ENGINEERING AND NANOTECHNOLOGY

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ACADEMIC YEAR: 2022-2023

1. Introduction

Plasmonics is a branch of photonics that deals with the interaction between an electromagnetic field and metals, focusing on the possibility of overcoming the problems related to the diffraction limit of light.[1]

The most common plasmonic materials are noble metals, such as gold and silver. They are widely used for plasmonic applications because of their large electrical conductivity and small ohmic losses. On the other hand, these materials are characterized by significant optical losses (large imaginary part of the dielectric function), by a low chemical and thermal stability, and the fabrication process of thin films could present some problems related to the high percolation threshold. [2]

For these reasons, in the recent years research on new noble metal-free plasmonic materials became fundamental. These novel plasmonic materials have attracted the attention of the researchers for the possibility of developing a new class of materials called metamaterials (MMs), which are structures artificially fabricated that cannot be found in nature, characterized by peculiar electromagnetic properties. An important sub-class of MMs, that has been explored in the last year for its optical properties, is the one of hyperbolic metamaterials (HMMs) [3]. HMMs are highly anisotropic structures with relatively simple geometry. The term "hyperbolic" is referred to the typical shape of the dispersion relation of light that can be achieved when a condition of dielectric anisotropy is satisfied.

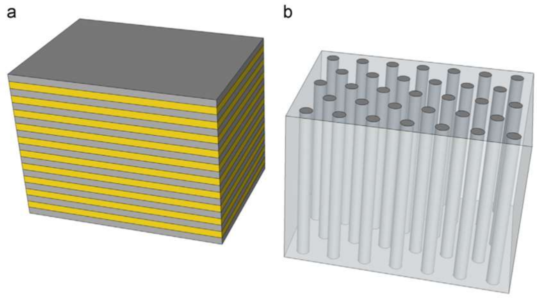

Figure 1 Schematic representation of the two possible configurations of HMMs: (a) multilayered structure, (b) nanorod array (b) [4]

The two most common structures adopted for the development of HMMs are:

- Multilayered structures, in which sub-wavelength metal and dielectric layers are periodically alternated. (Figure 1.a)
- Nanorod arrays, in which metallic nanorods are placed in a dielectric matrix separated by subwavelength lengths. (Figure 1.b)

The range of wavelengths in which the structure assumes a hyperbolic behavior is strongly affected by the materials selected for the development of HMMs. Indeed, transition metal nitrides and transparent conductive oxides can be used as plasmonic building blocks to promote the development of an hyperbolic behavior in the near-infrared (NIR) range, while III-V doped semiconductors, SiC and graphene favor this behavior in the far-infrared range.

One of the most promising noble melal-free plasmonic material is titanium nitride (TiN) [4], that belongs to the class of transition metal nitrides. TiN is characterized by good optical and electrical properties (i.e. relatively small negative dielectric permittivity, low interband losses, relatively high electron conductivity and mobility), good chemical and thermal stability and good compatibility with several transparent conductive oxides, such as Ta:TiO_2. For these reasons, TiN can be used to develop different noble-metal-free novel structures with the aim of exploiting the hyperbolic behavior for several plasmonic applications, such as high-resolution imaging.

During this master thesis work, multilayered structures based on TiN have been developed, with the aim to investigate the possibility to tune the optical properties of the system controlling the geometry (varying the order and the thickness of the layers), the materials selected (controlling the content of doping agent in the doped semiconductor used as dielectric component) and controlling the deposition condition of titanium nitride) and the temperature at which the structures have been fabricated. A novelty of this project consists in the choice of Ta:TiO_2 as the dielectric building block for this type of multilayered structures. Since it has a plasma wavelength in the IR range (around 4100 nm), its combination with a metal that shows a double-epsilon-near zero behavior could, in principle, extends the range of hyperbolicity of these structures to the IR range, due to an inversion of the behavior of the components of the multilayers.

2. Experimental techniques

All the samples produced during this work have been obtained through Pulsed Laser Deposition (PLD) using a Nd:YAG laser (with second harmonic at λ = 532 nm, repetition rate fp = 10 Hz and pulse duration ~ 6 ns). The apparatus used for the deposition is equipped with a vacuum pumping system, composed of a primary (Agilent TriScroll 600) and a turbomolecular (Pfeiffer Vacuum TMU 521) pump. The temperature of the substrates has been controlled by means of a substrate heater directly connected to the substrate holder, capable of heating the substrate up to 350°C. The samples have been deposited in vacuum or in presence of a controlled pressure using MKS Multi Gas Controller 647C. Targets of stoichiometric TiN (99% pure, with diameter of 1 inch and 2 inches), Ta:TiO_2 (with 5% of Ta in mass, with diameter of 2 inches) and Ta:TiO_2 (with 10% of Ta in mass, with diameter of 2 inches) have been used for the fabrication of the specimens. The target-to-substrate distance has been set to 5 cm. After the deposition, a thermal treatment in vacuum (10^{-5} Pa) at around 500°C, with a dwell time of 1 hour, has been performed on different samples. The morphology and the stoichiometry of the films deposited have been investigated by means of Scanning Electron Microscopy (Field Emission SEM, Zeiss Supra 40), Energy Dispersive X-ray Spectroscopy (detector for EDXS microanalysis by Oxford Instruments) and Raman spectroscopy (Renishaw InVia micro-Raman spectrometer equipped with an optical microscopy). The reflection of the samples has been analyzed through UV-Vis-NIR spectroscopy (Lambda 1050 UV/ViS/NIR spectrophotometer equipped with a Perkin Elmer 150 mm integrating sphere) and ellipsometry (J.A. Woollam Co. M2000 ellipsometer). Finally, electrical measurements have been performed by means of the four-probe Van der Pauw method (Keythley 2400 SourceMeter, for the generation of the current, and an Agilent 34970A as voltage meter. All the system is connected to a Keysight 34972A LXI Data acquisition unit)

3. Experimental results

To develop TiN-based multilayered structures, it has been necessary to investigate the effect of the deposition parameters on the morphology, optical and electrical properties of the single components of the system. For this reason, single layer reference samples of TiN and Ta:TiO_2 have been deposited with various thicknesses, down to values used in multilayers and characterized. Then two different sets of TiN-based multilayers have been fabricated focusing the attention on the effects of the deposition temperature (first set), the geometry and the materials selection (second set) on the optical properties of the structures.

3.1 Reference samples

Titanium nitride thin films, with thickness of 200 nm, have been deposited on silicon and glass substrate by means of PLD technique in low (0.1 and 0.4 Pa) and high (10^{-3} Pa) vacuum and in presence of a reducing atmosphere (1 Pa and 3 Pa of N_2-H_2) at room temperature and at 350°C. It has been decided to deposit TiN in low vacuum and in presence of N_2-H_2 to favor, according to a previous study carried out at the Nanolab laboratories, the development of a double-epsilon-near zero behavior that can allow to extend the range of hyperbolicity of Ta:TiO_2/TiN multilayers to the far-infrared range, due to an inversion in the typical behavior of the components of the structure.

An annealing in vacuum at around 500°C has been performed on selected samples to study its effect on the structure, optical and electrical properties of the samples produced.

The morphology of the films has been investigated by means of SEM, confirming the obtainment of compact, columnar, and adherent films. (Figure 2)

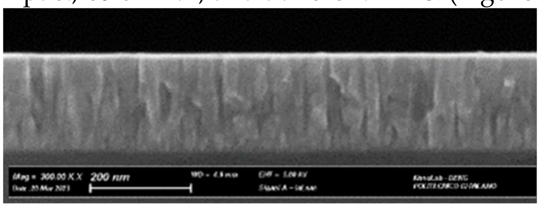

Figure 2 Example of cross-section image of a TiN thin film.

The characteristic sub-stoichiometric nature, in nitrogen, of TiN films has been confirmed by the presence of a broad acoustic band below 400 cm^{-1} in the Raman spectra of the samples analyzed. (Figure 3) Considering the films deposited in vacuum, their stoichiometry has not been significantly influenced by the substrate temperature and by the values of deposition pressure.

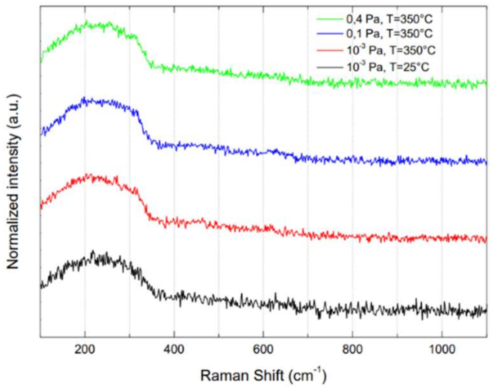

Figure 3 Raman spectra of TiN samples deposited in vacuum.

While, for the samples deposited in presence of N_2-H_2, a narrowing of the acoustic band has been noticed, meaning that the deposition in presence of N_2-H_2 promoted the incorporation of nitrogen in the films reducing the concentration of nitrogen vacancies (Figure 4).

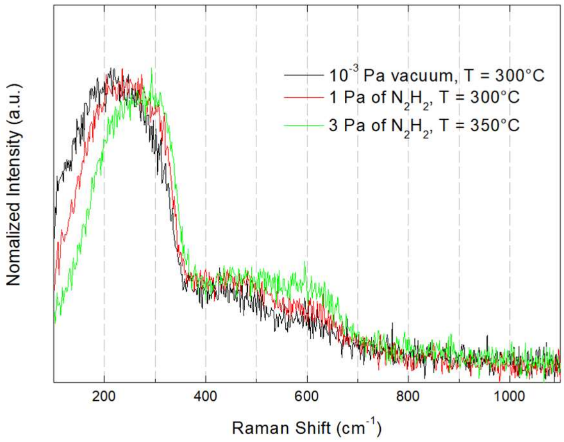

Figure 4 Comparison between Raman spectra of samples deposited in vacuum and with N_2H_2.

The thermal treatment performed on selected samples deposited in vacuum and in presence of N_2-H_2, caused a narrowing and a blue-shift of the acoustic band below 400 cm^{-1} with the respect to the as-deposited samples. The first effect could be related to the obtainment of a more ordered structure, while the second one, according to literature, could be associated to a partial oxidation of the film. In addition, it has been proved that the effect of annealing is not affected by a substrate temperature of 350°C.

The optical properties of TiN films have been investigated by means of UV-Vis-NIR spectroscopy, obtaining the values of reflectance for all the samples in a range of wavelengths between 250 nm and 2000 nm (Figure 5). Looking at the results, it has been possible to observe that the position of the minimum in reflectance, that is linked to the plasma frequency of the material, has not been influenced by the deposition pressure (for the samples deposited in vacuum) and by the substrate temperature. On the other hand, for larger wavelengths, it has been observed that an increase in the substrate temperature caused an increase in the values of reflectance, and an increase in the deposition pressure provoked a decrease in the reflectance, meaning that these two parameters can be used to control the metallicity of TiN films deposited in vacuum. Considering the samples deposited in N_2-H_2, it has been observed a red-shift of the position of the minimum and lower values of reflectance with the respect to the films produced in vacuum, meaning that the deposition of TiN in presence of N_2-H_2 leads to the obtainment of a weaker metallic behavior.

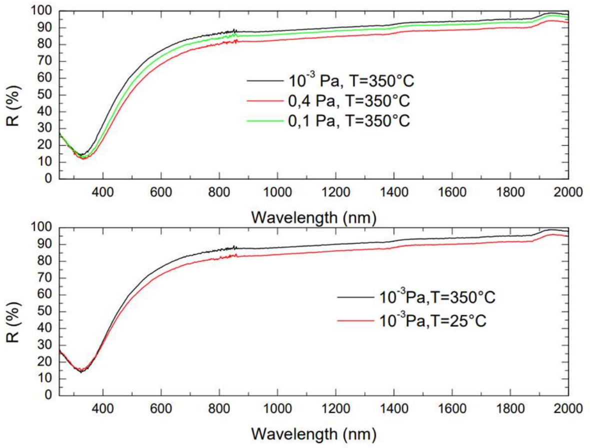

Figure 5 Reflectance curves of TiN samples deposited in vacuum.

The annealing treatment caused an increase in the position of the minimum and a reduction of the values of reflectance, highlighting a depletion of the metallic behavior of the films, that could be probably related to a phenomenon of oxidation occurred during the thermal treatment. The dielectric function ε of TiN films has been retrieved interpolating the data, obtained by means of ellipsometric measurements, with a model resulting from a combination of Drude and Lorentz ones. The plasma wavelength of TiN, computed as point in which the real part of ε is null, is equal to around 410 nm for all the samples deposited in vacuum and to 510 nm for the samples deposited in N_2-H_2. The data confirmed the results observed during the analysis of the reflectance curves, regarding the effect of the substrate temperature and deposition pressure/atmosphere on the optical response of TiN thin films. Due to technical problems related to the uniformity of the thickness of the samples deposited on glass substrate, electrical measurements have been performed only on few samples, but the data obtained confirmed the positive effect of the substrate temperature on the metallicity of TiN films. Indeed, an increase in the deposition temperature caused a decrease in the resistivity of the samples.

Ta:TiO_2 thin films with thicknesses of 20 nm and 200nm have been deposited on silicon and glass substrates at 350°C starting from Ta:TiO_2 targets with 5% and 10% of Ta. All the samples have been produced in presence of 1 Pa of O_2 to obtain a good transparent conductive oxide (TCO). A thermal treatment in vacuum at around 500°C has been performed on every samples deposited to promote the crystallization of Ta:TiO_2.

The morphology of the films has been investigated by means of SEM, confirming the obtainment of compact and adherent films.

The crystallinity of the samples has been assessed through Raman spectroscopy, highlighting that a deposition temperature of 350°C, which is close to the amorphous-crystalline transition temperature of Ta:TiO_2 (around 400°C), is enough to promote the crystallization of Ta:TiO_2 films of 200nm.

Looking at the results obtained (Figure 6), it has been possible to observe that the intensity of the characteristic signals of crystalline Ta:TiO_2, and so the degree of crystallinity, is dependent on the content of tantalum. The different position of the peak around 600 cm^{-1} suggests that the content of Ta can also affect the phase in which the material crystallize. In particular, the sample with 10% of Ta shows the typical signal of the anatase phase, while the one with 5% of Ta shows signals of the anatase and rutile phase, indicating a probable coexistence of these two phases.

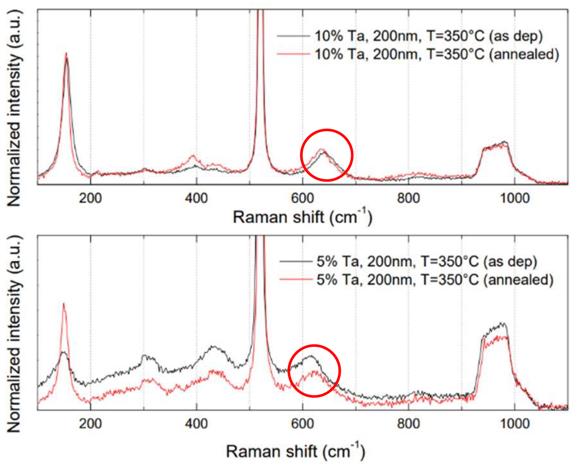

Figure 6 Raman spectra of Ta:TiO_2 samples before and after the annealing.

After the annealing, the Raman spectrum of the sample with 10% of Ta remained unchanged, while the one of the film with 5% varied.

This confirmed that the content of tantalum can influence the effects of the substrate temperature on the crystallization process of Ta:TiO_2 films. In particular, the sample with 10% of Ta was completely crystallized already after the deposition at 350°C, while the film with 5% of Ta

needed to be annealed in vacuum at 500°C to complete the process of crystallization.
This represents an important results because it has been verified the possibility of obtaining a crystalline $Ta:TiO_2$ film after the deposition without needing an annealing process. In addition, it has been verified that an increasing content of Ta caused a progressive blue-shift of the characteristic peak of $Ta:TiO_2$ at around 150 cm^{-1}.

3.2 $Ta:TiO_2$/TiN multilayers

A first set of multilayers (Figure 7), composed of TiN (deposited at 10^{-3} Pa) and $Ta:TiO_2$ (with 5% of Ta), have been deposited with the objective of investigating the effects of the substrate temperature and the order of the layers on the structure and on the optical response of the system. The samples have been deposited using a TiN target (diameter of 1 inch) mounted on a $Ta:TiO_2$ one (diameter of 2 inches). The thicknesses of the single layers have been maintained constant and equal to 20nm, with a number of layers equal to 10 and 11. On the samples produced, a thermal treatment in vacuum at 500°C has been performed.

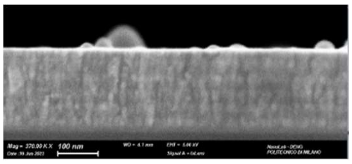

Figure 7 Example of cross-section image of a multilayered structure.

After the annealing, several detachments of the films have been observed only on the samples deposited at room temperature, meaning that an increase in the substrate temperature could promote the relaxation of the residual internal stresses induced during the deposition.
The crystallinity and the stoichiometry of the single layers have been assessed by means of Raman spectroscopy, highlighting the obtainment of sub-stoichiometric, in nitrogen, layers of TiN. (Figure 8) The typical signal of crystalline $Ta:TiO_2$ present at around 150 cm^{-1} is probably covered by the broad acoustic band of TiN, but signals at 400 cm^{-1} and 600 cm^{-1}, that could be related to the anatase phase of TiO_2, have been observed, meaning that the superficial layer of $Ta:TiO_2$ of the sample deposited at 350°C could be crystalline. After the annealing, the broad acoustic band of TiN blue-shifted, confirming the results of the characterization of the reference samples. The measurements of reflectance highlighted the presence of interference fringes due to the presence of several metal-dielectric interfaces. The position of the minimum and the values of reflectance are different with respect to the case of the single layer of TiN, meaning that the optical properties of TiN layer can be influenced by its implementation in a metal-dielectric multilayered structure.

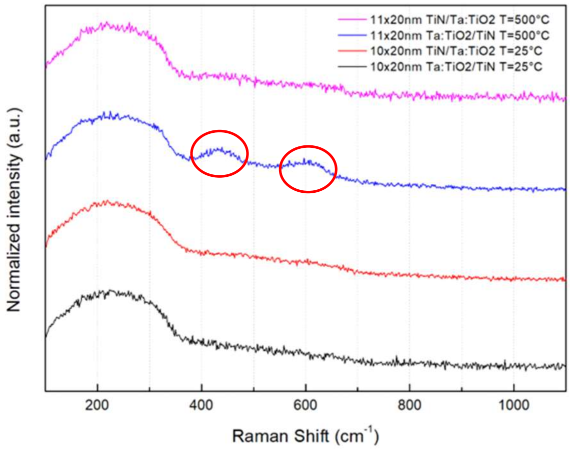

Figure 8 Raman spectra of $Ta:TiO_2$/TiN multilayers (as dep) deposited a different temperatures.

Executing simulations, based on the effective medium theory, it has been possible to assess that the structure should a hyperbolic behavior for wavelengths larger than 650 nm. A second set of multilayers (not shown) have been developed with the aim of investigating the effects of the materials selection and the geometry on the optical response of the systems. By means of several simulations, it has been possible to observe that the structures that showed the widest range of hyperbolicity were the ones in which the metal layers were thicker than the dielectric ones, independently on the metal and dielectric selected. For these reasons, the two most metallic TiN (in vacuum at 0.1 Pa and at 10^{-3} Pa) and the $Ta:TiO_2$ which crystallizes better (with 10% of Ta) during the deposition have been selected. All the depositions have been carried out at 350°C to exploit the positive effect of the substrate heater related to the adhesion of the films. The geometries explored during the experiments are:

- 30 nm of TiN + 20 nm of $Ta:TiO_2$.
- 20 nm of TiN + 10 nm of $Ta:TiO_2$.

The number of layers has been fixed to 11 to expose to the environment the most chemically stable material, the oxide. The morphology of the films has been investigated by means of SEM, confirming the obtainment of compact and adherent films, highlighting the separation of the different layers. By means of Raman spectroscopy, it has been possible to highlight the crystallization of the superficial layers of Ta:TiO_2, by the presence of signals that can be related to the anatase phase of TiO_2. During the analysis of the optical properties of the structures, it has been noticed that the values of reflectance were influenced by the thicknesses of the layers. In particular, increasing the thicknesses the position of the minimum shifted towards larger wavelengths and the values of reflectance were lower, confirming the possibility of tuning the optical properties of multilayered structures controlling their geometries. (Figure 9)

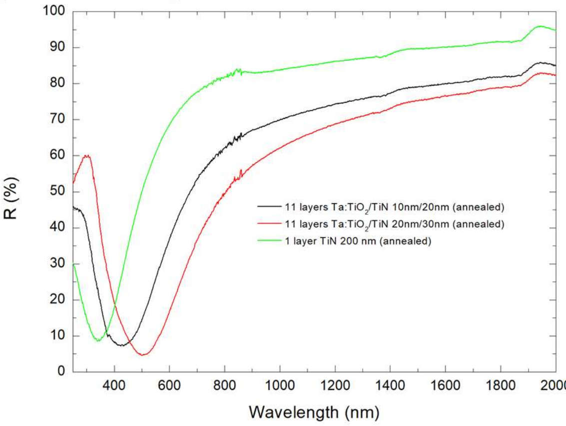

Figure 9 Comparison between reflectance curves of multilayers and a single layer of titanium nitride.

This trend of the reflectance has been highlighted also by several simulations, based on the transfer matrix theory, that have been executed using the data retrieved during the characterization of the reference samples.

4. Conclusions and future developments

The effects of the substrate temperature on the deposition of single layers of TiN and Ta:TiO_2 have been explored, highlighting the fact that a deposition temperature of 350°C is enough to promote the development of a stronger metallic behavior in TiN films and to promote the crystallization of Ta:TiO_2 films without needing a post-deposition thermal treatment. A probable partial relaxation of the internal stresses, induced during the deposition, has been observed in the samples deposited at around 350°C. The hyperbolic behavior of the different structures has been predicted by means of simulations, noticing that structures with metallic layers thicker than the dielectric ones can show a wider range of hyperbolicity. A geometry dependence of the optical response of multilayers has been observed through simulations and confirmed by experimental data.

Considering the results obtained during this work, the possibility of extending the use of the substrate heater for other materials and structures could be considered as possible future perspective. In addition, in future, a larger number of geometries should be explored to have a more complete understanding of the effects that the thickness of the layers has on the optical response of multilayered structures. In addition, the implementation of these structures in optical devices, such as hyperlens, should be considered. Moreover, the possibility of implementing double-epsilon-near-zero materials in HMMs should be investigated more deeply to enlarge the range of applicability of this type of structures. Lastly, IR optical measurements should be performed to investigate the properties and the hyperbolic behavior of this type of structure in this range of wavelengths.

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