Research Article

Tuning Metamaterials for Applications at DUV Wavelengths

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The unique properties of metamaterials, namely, their negative refractive index, permittivity, or permeability, have gained much recent attention. Research into these materials has led to the realization of a host of applications that may be useful to enhance optical nanolithography. A selection of materials has been examined both experimentally and theoretically to verify their support of surface plasmons, or lack thereof, in the DUV spectrum via the attenuated total reflection (ATR) method using the Kretschmann configuration. At DUV wavelengths, materials that were previously useful at mid-UV and longer wavelengths no longer act as metamaterials. Structured materials comprised of alternating layers of aluminum and aluminum oxide (Al_2O_3), as well as some other absorption-free dielectrics, exhibit metamaterial behavior, as do some elemental materials such as aluminum. These elemental and structured materials exhibit the best properties for use in plasmonic nanolithographic applications. Therefore, a simulator was created to examine material and thickness combinations to generate a tunable metamaterial for use in the DUV. A method for performing plasmonic interference lithography with this metamaterial has been proposed, with calculations showing the potential for half-pitch imaging resolution of 25 nm.

1. Introduction

A surface plasmon (SP) is an electromagnetic wave carried by free electrons that travels along the boundary between a conductor and a dielectric. Surface plasmons were first noticed experimentally in the early 1900s by Wood [1] as anomalous drops in the reflected intensity from metal-backed gratings, but it was not until the 1940s that Fano [2] linked this to earlier theory developed by Sommerfeld [3]. In the late 1950s, Ritchie [4] performed experiments on electron energy losses in thin foils, and Pines and Bohm [5–7] discovered that these losses were due to the excitation of conducting electrons, plasma oscillations they named plasmons [8]. In the 1960s, Kretschmann and Raether [9], as well as Otto [10], developed techniques to optically excite surface plasmons via attenuated total reflection (ATR). It was not until the early 1990s that exponential growth in plasmon research began [11].

In 2000, Pendry [12] showed that Veselago's [13] theoretical negative refractive index slab lens was realizable using a negative permittivity material instead, and that this near field imaging system was enabled by surface plasmons.

This discovery encouraged research into plasmonic lithography [14–17].

While the idea of Pendry's perfect lens is of importance and allows deep subwavelength imaging of arbitrary shapes, it requires a complex mask with feature sizes on the same order as those to be imaged. More recently, others have proposed the idea of maskless plasmonic interference lithography, in which two beams are input at opposite sides of a Kretschmann configured prism, creating two counter propagating surface plasmons, resulting in a standing wave [18, 19]. The pitch for this setup is shown in (1) and is dependent upon the permittivity of the prism, incident angle (resonance angle), and the incident wavelength [20]:

$$p = \frac{\lambda_0}{2\sqrt{\epsilon_d} \sin \theta}. \quad (1)$$

Much of this research has been performed at mid-UV wavelengths, as silver is a near ideal material for use in that spectrum. However, most currently lithography is performed in the DUV spectrum, and it is our goal to examine

FIGURE 1: Surface plasmon dispersion curves for Kretschmann ATR configuration, calculated using material properties for Al and SiO₂ from RIT material database [22].

FIGURE 2: Kretschmann configuration (left), Otto configuration (right).

metamaterials that could be used for plasmonic imaging in this regime.

2. Approach

The dispersion relation for surface plasmons can be obtained by solving the wave equation and is described well in [21]. The resulting surface plasmon dispersion relation for a single interface is

$$\beta = \frac{\omega}{c} \sqrt{\frac{\epsilon_m \epsilon_d}{\epsilon_m + \epsilon_d}}, \quad (2)$$

where β is the propagation constant, ω is the wave vector of the incident radiation, and ϵ_m and ϵ_d are the dielectric functions of the conductor and dielectric. It should be noted that this dispersion relation is only valid for TM polarization (also known as p polarization) states; surface plasmons are not excited by TE polarization. An example of the dispersion relation for SPs is shown in Figure 1.

Equation (2) shows that the propagation constant becomes asymptotic when the dielectric functions are equal

Layer Maker computes possible MIM stack combinations

FIGURE 3: Diagram representing Layer Maker application output.

and opposite in sign, for example, $\epsilon_m = -\epsilon_d$. This condition is known as the surface plasmon resonance (SPR). In Figure 1, the red air line represents the dispersion line for radiation in free space, while the SP dispersion curve for the air-metal interface is the light blue curve that lies to the right of it (same convention for glass). At frequencies far below the SPR frequency, the SP propagation constant is relatively small, meaning that the SP wavelength, $\lambda_{sp} = 2\pi / \text{Re}(\beta)$, is only slightly smaller than the incident radiation. As the frequency of the incident radiation increases to the surface plasmon resonance frequency, the propagation constant increases and approaches infinity at the SPR frequency, meaning that the SP wavelength becomes infinitesimally small. For real metals that are not perfect conductors and exhibit some absorption, the dispersion curves do not become entirely asymptotic, and the dispersion curve sharply moves back to a smaller propagation constant (longer wavelength).

It is apparent from the dispersion curves that a surface plasmon on a simple metal-dielectric interface cannot be excited by light due to the SP propagation constant always being larger than the wave vector of light in the dielectric. However, incident light can be phase matched with the SP by means of prism coupling, a technique referred to as ATR, using either the Kretschmann configuration [9], which has the prism and metal film in direct contact (Figure 2(a)), or the Otto configuration [10], in which a dielectric prism and metal are separated by an air gap (Figure 2(b)). In both configurations, phase matching is accomplished by varying the angle of incidence of the TM-polarized radiation, resulting in a sharp decrease in the reflected intensity at some angle beyond the critical angle. The phase matching occurs when the in-plane wave vector of the reflected beam along the metal surface is the same as the propagation constant; this relationship is shown in (3). The only propagation constants available are those that lie between the air and prism light lines (in Figure 1, this would be between air and glass)

$$k_x = k_0 n_p \sin \theta = \beta. \quad (3)$$

The surface plasmon dispersion equation shows that a negative permittivity material is needed in conjunction with a dielectric to support surface plasmons. We have previously shown that aluminum is one of the best candidates for use in the DUV spectrum [23]. However, while it is clear that these results demonstrate aluminum supports surface plasmons in the DUV, they need to be considered in conjunction with the plasmon dispersion equation for this ATR setup. Figure 1 shows the dispersion curves for an ATR configuration with an aluminum film and quartz prism.

FIGURE 4: ATR results for 7 nm Al, 27 nm Al_2O_3 , 7 nm Al stack (left), and single 20 nm Al layer (right).

FIGURE 5: Simulator flow chart.

FIGURE 6: Electric field intensity profiles below a 7 nm-27 nm-7 nm Al-Al₂O₃-Al stack (left) and 20 nm Al film (right) deposited on a quartz prism.

FIGURE 7: Electric field intensity profiles below 7 nm-34 nm-7 nm Al-Al₂O₃-Al stack (left) and 20 nm Al film (right) deposited on a sapphire prism.

Incident radiation of 193 nm corresponds to an angular frequency of $\sim 9.7 \times 10^{15} \text{ s}^{-1}$, which means that the accessible surface plasmons are of a wavelength very similar to that of the incident radiation ($\lambda_{\text{sp}} \sim 171 \text{ nm}$). Plasmonic interference lithography takes advantage of the fact that at the surface plasmon resonance, the SP wavelength is much smaller than the exciting wavelength. Therefore, a metamaterial needs to be designed to produce a surface plasmon resonance at the desired input frequency.

Pendry has previously demonstrated that it is possible to create a structured material that can be tuned to provide the desired plasma response [24, 25]. Pendry has more recently shown that this structure needs not to be comprised of wires, but that holes in a thin metal film can be designed to provide surface plasmons with arbitrary dispersion [26]. Others have shown that an even simpler design of a layered metal-insulator-metal (MIM) stack can be used to accomplish this [27–31]. Thus, an MIM stack should be examined to provide the desired dispersion characteristics.

Since aluminum is one of the best plasmonic materials in the DUV, and Al₂O₃ is a relatively high-index, absorption-free dielectric, a layered Al-Al₂O₃ system will be examined. A simulator was created to generate and analyze multilayer MIM stacks in order to obtain the largest propagation constants possible, resulting in the shortest plasmon wavelength.

The first module of the simulator is the Layer Maker application, which generates the multilayer stacks to be examined. The refractive index and absorption coefficients of the superstrate (prism), metal, dielectric, and substrate can be input, as well as the maximum total stack thickness to be allowed, the maximum dielectric thickness, and the maximum metal thickness allowed (this is the overall maximum metal thickness, not one individual layer thickness, as it is known in the Kretschmann configuration that if the metal is too thick, SPs cannot couple through it). This application then outputs two files containing all layer combinations within the boundary conditions specified. One file is a MySQL table that will be linked to the output of

TABLE 1: Joined data in MySQL.

Layer ID	Layers	Metal thick (nm)	Metal count	Dielectric thick (nm)	Dielectric count	Angle (deg)	Reflectance	Beta
15127	3	5	2	28	1	87.51	0.0042	50738563
15156	3	5	2	29	1	87.51	0.0682	50738563
15098	3	5	2	27	1	87.02	0.1021	50717534
15185	3	5	2	30	1	87.02	0.2338	50717534
17574	3	6	2	27	1	87.02	0.0072	50717534
17551	3	6	2	26	1	86.52	0.0358	50692685
17597	3	6	2	28	1	86.52	0.1171	50692685
15214	3	5	2	31	1	86.02	0.3819	50664018
15069	3	5	2	26	1	85.52	0.2362	50631535
17620	3	6	2	29	1	85.52	0.2723	50631535
19837	3	7	2	26	1	85.52	0.0034	50631535
19856	3	7	2	27	1	85.52	0.0898	50631535
15243	3	5	2	32	1	85.03	0.4932	50595239
17528	3	6	2	25	1	85.03	0.1433	50595239
19818	3	7	2	25	1	85.03	0.0348	50595239
17643	3	6	2	30	1	84.53	0.4044	50555133
19875	3	7	2	28	1	84.53	0.2368	50555133
21971	3	8	2	26	1	84.53	0.0294	50555133
15040	3	5	2	25	1	84.03	0.3425	50511218
15272	3	5	2	33	1	84.03	0.5753	50511218
21954	3	8	2	25	1	84.03	0.0040	50511218
21988	3	8	2	27	1	84.03	0.1495	50511218
15301	3	5	2	34	1	83.54	0.6369	50463500
17666	3	6	2	31	1	83.54	0.5052	50463500
19894	3	7	2	29	1	83.54	0.3722	50463500
17505	3	6	2	24	1	83.04	0.2461	50411980
22005	3	8	2	28	1	83.04	0.2939	50411980
23936	3	9	2	26	1	83.04	0.0465	50411980
15330	3	5	2	35	1	82.54	0.6840	50356665
17689	3	6	2	32	1	82.54	0.5813	50356665

the other applications via an identity string assigned to each MIM stack. The second file contains a machine readable instruction file for the second application. An example of this table is shown in Figure 3. It should be noted that this application generates stacks comprised of many layers, not simply a 3-layer MIM stack. We are only examining a 3-layer stack here as it is most likely the easiest to fabricate.

The second application is the Matrix Material Calculator (MMC) and is written in MATLAB. It reads the instruction file from the Layer Maker application and calculates reflection profiles through angle for each generated stack. These calculations are performed using matrix methods described by Macleod [32], shown in (4) through (10). The substrate is air, and the initial medium is the quartz prism. The characteristic admittance of each layer is represented as y_j and consists of the optical parameters of the layer. The oblique optical admittance is represented by η and must be calculated for each polarization state. The film phase factor is δ . The amplitude reflection coefficient ρ can be calculated from the characteristic matrix of the film stack (4), and from this result, the reflectance can be obtained (shown in (10)). With oblique incidence and absorbing materials, care must be taken to ensure that the solutions for η for TE polarization

states and δ are in the fourth quadrant to obtain the correct solution (positive real, negative imaginary):

$$\begin{bmatrix} B \\ C \end{bmatrix} = \left\{ \prod_{j=1}^q \begin{bmatrix} \cos \delta_j & \frac{i \sin \delta_j}{\eta_j} \\ i \eta_j \sin \delta_j & \cos \delta_j \end{bmatrix} \right\} \begin{bmatrix} 1 \\ \eta_{\text{sub}} \end{bmatrix}, \quad (4)$$

$$y_j = n - ik, \quad (5)$$

$$\eta_{j_s} = \sqrt{n_j^2 - k_j^2 - n_0^2 \sin^2 \theta_0 - 2in_j k_j}, \quad (6)$$

$$n_{j_p} = \frac{y_j^2}{\eta_{j_s}}, \quad (7)$$

$$\delta_j = \frac{2\pi d}{\lambda} \sqrt{n_j^2 - k_j^2 - n_0^2 \sin^2 \theta_0 - 2in_j k_j}, \quad (8)$$

$$\rho = \frac{y_0 B - C}{y_0 B + C}, \quad (9)$$

$$R = \rho \rho^*. \quad (10)$$

The third application is the Beta Profiler. It analyzes the reflection profiles and calculates the angle at which the

reflection minimum occurs, the reflectance value, and the value of the propagation constant (from (3)). This data is also stored in a MySQL table. By itself, this data is not inherently useful. However, using join statements in MySQL, this data can be merged with the table from the Layer Maker application and sorted to display results that are useful.

Since outputs of the MMC and the Beta Profiler are stored in a MySQL databases it is possible to quickly sort through the data to find optimal cases and analyze the results. An example of a joined output from the Layer Maker and Beta Profiler is shown in Table 1.

The fourth application is the RT Profiler, which is uses the Layer ID to test cases that appear promising. The results shown in Figure 4 are the output of the RT Profiler application. They show that a 3-layer stack comprised of 7 nm-27 nm-7 nm of Al-Al₂O₃-Al yields a metamaterial with a shorter plasmon wavelength than is capable with just aluminum (124 nm compared to 171 nm). A summary of the simulator is shown in the flow chart in Figure 5.

Since the final layer of the tunable metamaterial proposed is Al, it is understood that it will oxidize. The Layer Maker application has been modified to allow an asymmetric stack to be simulated. This makes it possible to simulate our metamaterial stack with a surface oxide layer present, or with a capping material comprised of some other element that may offer more desirable optical properties than an aluminum oxide.

There are several benefits of this simulation approach. Firstly, this matrix method of calculation provides fast results. Simulations of 1 single-layer ATR stack in FDTD software took on the order of a minute to complete. Using this matrix method-based simulator, 50,000 different thin film stack combinations were completed in approximately 90–120 minutes. Secondly, it is quite flexible. Any optical constants desired can be input, and it has been modified further to allow for an asymmetric stack to be input. It has also been modified to allow the optical parameters and thicknesses to vary in order to help model errors that will be seen during fabrication. The joined output data allows one to see the fabrication tolerances allowed to achieve an acceptable result.

The thin film matrix calculations used throughout this document can also be used to calculate the electric field intensity below the stack, which would be representative of imaging possible for plasmonic interference nanolithography. Results for the configurations in Figure 4 are shown in Figure 6. The resulting pitches of 62 nm and 84 nm are similar to those calculated using (1).

If a higher index prism is used, an even smaller plasmon wavelength can be achieved. Figure 7 shows the electric field intensity for a 7 nm-34 nm-7 nm Al-Al₂O₃-Al stack using a sapphire prism ($n = 1.92$), resulting in a 50 nm pitch (the ATR profile is nearly identical to that for the quartz prism example shown in Figure 4). The resulting pitch for the 20 nm Al film with the sapphire prism is still nearly identical to that with the quartz prism, due to the fact that the higher index of the prism is offset by a 10° shift, from ~46° down to ~36°, in the resonance angle.

3. Conclusion

Little research in metamaterials and plasmonics has been done in the DUV spectrum. This paper demonstrates a simulator developed using thin film matrix methods to create tunable metamaterials for the DUV spectrum. It showed that a quartz prism coated with a 7 nm-27 nm-7 nm Al-Al₂O₃-Al thin film stack or a sapphire prism coated with 7 nm-34 nm-7 nm Al-Al₂O₃-Al is possible solutions, providing more desirable propagation constants, and thus shorter plasmon wavelengths for use in DUV plasmonic interferometric imaging.

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