Controlling the optical parameters of self-assembled silver films with wetting layers and annealing

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\textbf{ABSTRACT}

We investigated the influence of presence of Ni and Ge wetting layers as well as annealing on the permittivity of Ag films with thicknesses of 20, 35 and 65 nm. Most of the research on thin silver films deals with very small (\textlessthan 20 nm) or relatively large (\textgreet 50 nm) thicknesses. We studied the transition region (around 30 nm) from charge percolation pathways to fully continuous films and compared the values of optical parameters among silver layers with at least one fixed attribute (thickness, wetting and capping material, post-process annealing). Our study, based on atomic force microscopy, ellipsometric and X-ray photoelectron spectroscopy measurements, shows that utilizing a wetting layer is comparable to increasing the thickness of the silver film. Both operations decrease the roughness-to-thickness ratio, thus decreasing the scattering losses and both narrow the Lorentz-shaped interband transition peak. However, while increasing silver thickness increases absorption on the free carriers, the use of wetting layers influences the self-assembled internal structure of silver films in such a way, that the free carrier absorption decreases. Wetting layers also introduce additional contributions from effects like segregation or diffusion, which evolve in time and due to annealing.

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1. Introduction

Thin silver films are used in sensor, plasmonic and metamaterial applications, provided that they have both low scattering and ohmic losses [1–14]. Scattering losses are reduced in metal layers if evaporated on polished substrates with low roughness (achievable value for SiO\textsubscript{2} is 0.3 nm roughness root mean square – RMS). Even better results can be achieved when the use of wetting layer promotes adhesion between metal particles and the substrate and thus prevents island growth. To block the Volmer-Weber growth, a number of wetting interlayers, like Ge, Ni, Ti, Cr or Cu were introduced [2–4,7,9–14]. The seed layer approach leads to the reduction of the surface roughness of deposited films and allows to acquire continuous Ag layers, even if the thickness is lower than 30 nm. RMS surface roughness of 10 nm-thick Ag films equals only 0.4; 0.9; and 2.0 nm for Ge, Ni and Ti wetting layers, respectively [10]. Germanium wetting layer is the most efficient in reducing scattering losses by smoothing the surface of silver films due to greater adhesion of Ag to Ge than that of Ag to fused silica — it causes low Ag adatom surface diffusivity [8]. However, this high adhesion of Ge to Ag also induces segregation of Ge atoms into Ag grain boundaries as well as film free surface. That results in a considerable increase of specific resistivity and limits the potential use of Ag films deposited on Ge wetting layer in plasmonic applications [13]. Moreover, the use of a segregating material may introduce new bands to the permittivity of a silver system, while increasing or decreasing the primary ones [13,14]. These new contributions may be tailored by temperature treatment (e.g. cooling the substrate in the deposition process) or the use of capping layers of another segregating material, such as Al\textsubscript{2}O\textsubscript{3} [13].

In this work, we discuss the influence over time of wetting layers on the crystallinity-induced permittivity of silver films with different thicknesses. Application of annealing allowed to control the self-assembly of the silver layers and in turn the additional contributions from the wetting films. The undesired influence of wetting on the primary permittivity components, like the Drude-Lorentz free carrier absorption, could also be mitigated. We chose to examine the permittivity of 20 and 35 nm-thick silver layers since this thickness range is not yet fully investigated. For the first wetting layer, we chose Ni, because of the good smoothing performance and minimal impact on the low-frequency resistivity [10] as well as weak solubility in silver [15]. For the second wetting layer, we chose Ge because of excellent smoothing performance [2] and the fact that it is most commonly used. For protection against cor-

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erosion we chose LiF to serve as capping layer, since it is easy to sputter and, unlike Al₂O₃, exhibits no segregation in silver.

The permittivity values of silver most commonly employed in contemporary numerical simulations (e.g., [16–18]) are usually the ones determined by Johnson & Christy [19] or in the papers collected by Palik [20] and do not comprehend the vast range of Ag films grown in different ways. Even more recent attempts to re-evaluate the dielectric function of silver in the variable range on discontinuous layers with thicknesses below 20 nm [1,21–23], fully continuous layers with thicknesses 100 nm or greater [24,25] or investigate similar to the ones already researched in order to evaluate the correctness of previous results [26]. However, in case of silver layers grown on wetting films, only the permittivity values for Ag grown on Au nanoparticles have been reported [27]. Here we provide silver permittivity values for use in simulations of silver grown on SiO₂ substrates with Ge or Ni interlayers.

2. Materials and methods

All films were deposited from fabmate or tungsten crucibles using PVD75 Lesker e-beam evaporator, on fused silica substrates with RMS roughness equal to 0.3 nm. The purity of the evaporation materials was 4N for silver, 4.5N for nickel, 5N for germanium and 3N for LiF. Before evaporation, substrates were cleaned with argon flow at 2 bar pressure. Ni and Ge were evaporated at an average deposition rate of 0.5 Å/s to form a 2 nm-thick wetting layer. Silver films of thickness 20, 35, and 65 nm were evaporated at an average deposition rate of 2 Å/s either directly on SiO₂ substrates or on Ge or Ni wetting interlayers. LiF was evaporated at an average deposition rate of 1 Å/s to form a 3 nm-thick capping layer. Deposition rate and total film thickness were monitored by two quartz weights inside the deposition chamber. Then, film thicknesses were verified by Dektak 6M stylus profiler. The pressure in the vacuum chamber was kept below 5 × 10⁻⁵ Torr during the whole deposition process. The crucible-substrate distance was 40 cm.

Roughness measurements were performed using NT-MDT and AIST-NT atomic force microscopes (AFM). The values of roughness RMS as well as average surface grain size were determined using Gwyddion (http://gwyddion.net) software.

Ellipsometric azimuths Ψ and Δ of fabricated samples were measured in the UV–VIS–MIR spectral range (0.06–6.5 eV) for three angles of incidence (65°, 70° and 75°) by the use of two instruments: V–VASE (J.A. Woollam Co., Inc.) in the UV–VIS–NIR and Sendira (Sen-tech GmbH) in the MIR. The complex dielectric functions of Ag layers were extracted using a layered model of the samples. The optical constants of the Ni wetting layer were determined in a separate experiment. Ge atoms exhibit intense segregation in silver films, therefore no independent Ge layer was considered in the model. The permittivities of silver films were then interpreted in terms of the Lorentz, Drude-Lorentz and Cody-Lorentz oscillator models. The Cody-Lorentz oscillator is commonly used to model the permittivity of semiconductors, however, the shape of modified Lorentz oscillator used by Rioux et al. [28] to reproduce the permittivity of silver at wavelengths below 320 nm is very similar to the Cody-Lorentz shape. Hence, the Cody-Lorentz oscillator was used here in conjunction with an additional tiny Lorentz oscillator to model the permittivity of silver below 320 nm. The differences in the values of permittivity obtained using both models are negligible except for wavelengths shorter than 250 nm, where the Ψ and Δ azimuths are subject to large noise, but even so, the discrepancy is rather small (see Fig. S1 in the Supporting information for details). Electron energy loss function (ELF) was calculated from the permittivity values using the following formula: \( LF = -\text{Im}(\varepsilon^{-1}), \) where \( \varepsilon \) is the complex permittivity of the layer.

The XPS measurements were performed at base pressure ≤ 2·10⁻¹⁰ mbar. Monochromatic radiation from Al Kα source (\( h\nu = 1486.6 \text{ eV} \)) was used to excite photoelectrons, the incidence angle was 55°. Photoemission spectra were recorded using VG Scienta R3000 hemispherical analyser oriented perpendicular to the samples’ surface. The XPS data were recorded from all of the elements found at the surface with the energy resolution set to 100 meV with the exception of lithium. The XPS data recordings were interlaced by Ar ion etching in order to study the chemical composition of subsequent sublayers. The energy of Ar ions was 4 keV and the incidence angle was 69°. Ion beam scanned the area of 4 × 4 mm in order to etch the analysed surface homogeneously. The concentrations of elements were estimated by fitting the most intensive peaks to Gauss-Lorentz shapes by using CasaXPS® software.

3. Results and discussion

3.1. Dependence of Ag film permittivity on thickness and roughness

Fig. 1 presents real (a) and imaginary (b) parts of permittivity of 20 and 35 nm-thick silver films in comparison to those of a fully continuous 65 nm-thick film. The most distinctive discrepancy is observed in the Lorentz-shaped peak in the imaginary part as well as the Drude term present in both real and imaginary parts. In most papers, e.g., [29,30], the Lorentz-shaped peak is attributed to the interband transitions at the 1 point in the Brillouin zone. However, while most theoretical approaches can predict the existence of this peak, none of them is able to exactly determine its value. In our case, for the thinnest, 20 nm-thick layer, the Lorentz-shaped band is centered at 378 nm and with the increase of silver thickness, a blueshift of this band is observed. Furthermore, the band gets narrower and the value of the maximum diminishes – from 0.75 in the case of 20 nm-thick film to 0.4 for the 65 nm-thick film. This correlates to the RMS-to-thickness ratio presented in Table 1. For the 20 nm film, the RMS-to-thickness ratio is most profound, implying that a large part of the layer is composed of narrow hills, where energy bands are sparse and shifted with respect to those of the bulk material. This also indicates an additional contribution from the intraband transitions. Moreover, those narrow hills increase the range of wavevectors accessible to surface plasmon-polaritons (SPP), allowing light to be coupled into SPP waves. Thus we interpret that the shape of the Lorentz band is intrinsically connected to the RMS-to-thickness ratio and originates not only from the contribution of the interband transitions at the L point in the Brillouin zone, but also from the intraband transitions as well as surface plasmon-polariton excitations. For thicker layers, the RMS-to-thickness ratio is lower and thus intraband transitions and localized plasmon coupling are limited. This results in narrowing and diminishing of the Lorentz-shaped band. For the 65-nm thick layer, the peak is barely observable, but on the other hand the maximum value of the Cody-Lorentz-shaped peak centered at 277 nm increased from 3.52 to 3.79. This suggests, that for very thick layers, the band structure at the L point resembles the band structure at other points in the Brillouin zone, at which the interband transitions contribute to Cody-Lorentz-shaped peak. We believe, however, that this is not strictly connected to the layer thickness, but rather to the RMS-to-thickness ratio corresponding to crystallinity.

To further investigate the impact of Ag roughness on the values of permittivity, we have used the RMS parameter of the 20 nm-thick silver film to split the silver film in the theoretical model into two sublayers. The top sublayer with triangular periodic roughness of height equal to the RMS value incorporates air to an intermix layer with silver content of 50% (the Bruggeman Effective Medium
Approximation – BEMA), so that in the bottom Ag sublayer roughness is lower (see Fig. 2). We have then extracted the value of permittivity only for the latter one. The result is presented by the black dotted curves on Fig. 1ab. The imaginary part of permittivity for the sublayer with limited roughness, although the layer is thinner than 20 nm, approaches the one of 65 nm-thick silver film in the UV range, where the Lorentz and Cody-Lorentz bands are centered. Applying the same procedure to the 65 nm-thick film does not change its permittivity, thus we can assume that the discussed effect does not result from the boundary conditions in Maxwell equations. Modifying the height and composition of the intermix sublayer (in the case of 20 nm-thick film) preserves the shape and position of the Lorentz peak, while switching the BEMA to the Maxwell-Garnett model does not (see Fig. S2 in the Supporting information for details). Overall, this is another claim confirming the intrinsic dependence of the Lorentz and Cody-Lorentz bands on the RMS-to-thickness ratio.

Increasing thickness also increases absorption on the free electrons, what is represented by more negative value of the real part of the permittivity. This comes to no surprise, since with the increased

### Table 1

Values of the roughness RMS, RMS-to-thickness ratio and the average surface grain size as well as the free electron lifetime for selected samples. The RMS and average grain size were determined using AFM. The RMS-to-thickness ratio was calculated by dividing the RMS factor by the total thickness of the silver layer. The free electron lifetime was derived from the ellipsometry measurements. If the sample has two τ values then the ones after slash are derived from the measurements performed two months after deposition.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Roughness RMS [nm]</th>
<th>RMS-to-thickness ratio</th>
<th>Average grain size [nm]</th>
<th>Free electron lifetime τ [fs]</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂/20 nm Ag</td>
<td>2.4</td>
<td>0.120</td>
<td>47</td>
<td>14.44 ± 0.34</td>
</tr>
<tr>
<td>SiO₂/35 nm Ag</td>
<td>3.1</td>
<td>0.088</td>
<td>58</td>
<td>15.19 ± 0.29</td>
</tr>
<tr>
<td>SiO₂/65 nm Ag</td>
<td>3.2</td>
<td>0.049</td>
<td>91</td>
<td>22.80 ± 1.00</td>
</tr>
<tr>
<td>SiO₂/2 nm Ni/20 nm Ag/3 nm LiF</td>
<td>1.3</td>
<td>0.065</td>
<td>32</td>
<td>10.19 ± 0.23</td>
</tr>
<tr>
<td>SiO₂/2 nm Ni/35 nm Ag/3 nm LiF</td>
<td>2.0</td>
<td>0.057</td>
<td>35</td>
<td>12.08 ± 0.27</td>
</tr>
<tr>
<td>SiO₂/2 nm Ni/20 nm Ag/3 nm LiF/100 °C</td>
<td>1.5</td>
<td>0.075</td>
<td>36</td>
<td>8.40 ± 0.12</td>
</tr>
<tr>
<td>SiO₂/2 nm Ni/35 nm Ag/3 nm LiF/100 °C</td>
<td>2.1</td>
<td>0.060</td>
<td>40</td>
<td>5.23 ± 0.11</td>
</tr>
<tr>
<td>SiO₂/2 nm Ge/20 nm Ag/3 nm LiF</td>
<td>0.5</td>
<td>0.025</td>
<td>19</td>
<td>5.20 ± 0.03/4.69 ± 0.04</td>
</tr>
<tr>
<td>SiO₂/2 nm Ge/35 nm Ag/3 nm LiF</td>
<td>0.6</td>
<td>0.017</td>
<td>21</td>
<td>6.23 ± 0.06</td>
</tr>
<tr>
<td>SiO₂/2 nm Ge/20 nm Ag/3 nm LiF/100 °C</td>
<td>0.9</td>
<td>0.045</td>
<td>23</td>
<td>5.81 ± 0.04/4.32 ± 0.04</td>
</tr>
<tr>
<td>SiO₂/2 nm Ge/35 nm Ag/3 nm LiF/100 °C</td>
<td>0.8</td>
<td>0.022</td>
<td>24</td>
<td>9.12 ± 0.14</td>
</tr>
<tr>
<td>SiO₂/2 nm Ge/20 nm Ag/3 nm LiF/300 °C</td>
<td>1.2</td>
<td>0.060</td>
<td>26</td>
<td>5.28 ± 0.05</td>
</tr>
</tbody>
</table>

Fig. 1. Real (a) and imaginary (b) parts of permittivity of a 20, 35 and 65 nm-thick silver films deposited directly on polished SiO₂ substrates without a capping layer (solid curves) as well as with a 3 nm-thick LiF capping layer (dashed curves). The black dotted curves represent permittivity for the 20 nm-thick Ag layer with extracted surface roughness. c – Electron energy loss function of the 20, 35 and 65 nm-thick silver films without capping layers.

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thickness, the probability of an electron reaching the surface is lowered, and with the reduced RMS-to-thickness ratio, the electrons are less likely to scatter on the surface details. Thus, free electron lifetime $\tau$ increases.

The impact of the RMS-to-thickness ratio on the permittivity of the silver films is most easily observed in the function of electron energy loss. The LF essentially determines the screened plasma frequency $\omega_p$ of the material. Fig. 1c presents the loss function of 20, 35 and 65 nm-thick silver layers deposited directly on SiO$_2$ substrates with no wetting or capping layers. All peaks are centered at 326 nm, which means that the plasma frequency of all silver films remains constant. However, with decreasing thickness, the peak diminishes. It means that smaller number of atoms contribute to the plasma frequency. In other words, lower value of this peak means that more non-silver atoms are detected. Thin layers have large RMS-to-thickness ratio, and so, deep valleys in the film structure might be present. As such, the air filling these valleys does not contribute to the plasma-frequency peak at 326 nm, causing the $\omega_p$ peak to diminish. It is worth noting, that the differences in the values of the loss function derived from the effective permittivity of investigated samples and the ones obtained from permittivities of silver films with extracted roughness are very small and the discussed tendencies are the same. That is why further analysis will be performed with the values of the loss function derived from the effective permittivities.

Since all investigated silver films have been deposited using e-beam PVD, they are polycrystalline. Thus, their permittivity differs vastly from the permittivity of Ag single crystal measured by Stahrenberg et al. [31]. The real part of permittivity of our films is greater in the UV, but lower in the visible spectrum, while the imaginary part is lower in the UV and exhibits a resonance connected to the RMS-to-thickness ratio which is not present in the measurements performed by Stahrenberg et al.

Thin silver films exhibit high thermal instability. 20 nm-thick layer disintegrates into a discontinuous island matrix immediately when reaching 300 °C [32,33]. However, even when stored for a significant amount of time (years) at room temperature, it also becomes discontinuous. During annealing, silver layers are more prone to oxidation than at room temperature. To avoid corrosion, the next examined samples were covered with 3 nm-thick LiF protective overlayer. Our results for 35 and 65 nm-thick silver samples with LiF overlayer (Fig. 1ab) prove that the influence of lithium fluoride on the permittivity of Ag films is negligible.

### 3.2. Influence of Ni wetting layer on the permittivity of Ag film

The use of Ni wetting film has decreased the surface horizontal grain size and the roughness of Ag layers (see Table 1), so that the RMS-to-thickness ratio of both 20 and 35 nm-thick Ag films deposited on Ni dropped below the value of bare 35 nm-thick silver layer, but is still greater than the value of 65 nm-thick layer. Fig. 3 presents real (a) and imaginary (b) parts of the permittivity of 20 and 35 nm-thick silver layers deposited on Ni wetting films capped with LiF overlayer, without (solid curves) and with annealing (dashed curves) at 100 °C for 30 min immediately after removing them from the deposition chamber. The Ni wetting film has narrowed and blueshifted the Lorentz-shaped interband transition peak of the 20 nm-thick silver layer, so that it resembles the one of 35 nm thickness, which should not surprise considering the reduction of RMS-to-thickness ratio. All silver films deposited on Ni wetting layer, except for the annealed 35 nm-thick one (Fig. 3c), have their plasma frequency shifted by 2 nm towards shorter wavelengths with respect to those without any wetting layer (Fig. 1c). This small blueshift may be a result of Ni atoms diffusion and/or segregation [34] in the silver films structure. Drude component of the permittivity significantly lower than that of layers without Ni interlayer, explains this tiny effect.

Annealing the 35 nm-thick silver sample at 100 °C has almost no influence on the plasma frequency or permittivity in the UV and visible range, same as in the case of annealing the non-wetted 35 nm-thick silver film (see Fig. S3 in the Supporting information). The discrepancy in the Drude term becomes noticeable at wavelengths around 4 μm and for this thickness, the free carrier absorption increases. To understand why it is so, we need to discuss several phenomena connected to the annealing process. The first one is that during annealing the films surface becomes more rough (see Table 1) due to the greater amount of larger nanocrystals [35]. This however, would rather increase the scattering of the free electrons on the surface, thus limiting the Drude component. Also, with increased temperature, the thermal energy of Ni atoms would be greater, increasing the diffusion and segregation into the silver film. This would also contribute towards decreasing the Drude term, because the free electrons would scatter on Ni atoms. However, we believe that in the case of 35 nm thick layer, the energy barrier for Ni atoms to migrate to the skin depth of silver, which is around 15 nm [36] is still greater than their thermal energy. Lastly, the melting point of smaller crystals in the film is lower than the
melting point of the larger ones [37,38]. Therefore, during annealing small crystals merge and form bigger ones [35,37,38] and so the number of the grain boundaries diminishes. With less grain boundaries, free electrons scatter less and thus the Drude component increases, as is observed for this sample. For bulk silver, annealing at 100 °C would probably not have any significant impact, but the melting temperature of thin films is much lower than the one of bulk materials [32,33]. Therefore, in case of nm-thick films the effect of annealing-induced grain growth provides a noticeable change in the optical parameters.

The case of 20 nm-thick films is quite different. While the influence of annealing on the permittivity in the UV and visible range is still negligible, it decreases the Drude term as well as the plasma frequency peak in the loss function spectrum. Though all of the effects described above contribute, the diffusion-segregation mechanism plays a more significant role. Since the silver layer is thinner, the energy barrier for Ni atoms to migrate to the skin depth of silver is lower. Apart from that, as the melting temperature decreases with the layer thickness, the 20 nm-thick film at 100 °C should be in a more liquidlike state than the 35 nm-thick film at the same temperature. Thus, Ni atoms migrate more easily into the silver structure, decreasing electron free lifetime \( \tau \) and diminishing the plasma frequency peak.

Annealing the 20 nm-thick Ag layer deposited directly on SiO\(_2\) substrate at 300 °C leads to an instantaneous droplet formation. Annealing the Ni-wetted 20 nm-thick silver film at the same temperature does not cause such disintegration. This is proven by identical values of permittivity for both the Ni-wetted silver sample annealed at 300 °C and the one annealed at 100 °C, whereas annealing the non-wetted 20 nm-thick Ag film at 100 °C for the same duration (30 min) results in slow-paced disintegration into droplets. Provided that the rise of the melting temperature of Ni-wetted silver film with respect to the one deposited directly on SiO\(_2\) substrates does not result simply from larger grain size in the depth of the film, there must be an additional contribution to the melting activation energy originating from the specific interactions of Ni atoms with Ag grains at the interface or segregated/diffused into the silver film. This is confirmed by the AFM measurements, which indicate that Ag films on Ni wetting layer have a lower grain size than non-wetted Ag films.

3.3. Influence of Ge wetting layer on the permittivity of Ag film

The use of Ge wetting layer decreases the surface roughness of the silver films fivefold, which is two times better than Ni (Table 1). It also decreases the mean surface grain size to around 20 nm. Fig. 4 presents the real (a) and imaginary (b) parts of permittivity as well as the loss function (c) of different Ag layers deposited on Ge wetting layers. Unless stated otherwise, ellipsometric and XPS measurements of these samples were performed exactly 10 days from the deposition process. For every Ag layer deposited on Ge interlayer, the Drude term observable well in the long wavelength range of the real part of permittivity is even lower than for those deposited on Ni interlayer. This is the result of segregation, as Ge atoms in the structure of Ag films are the scattering seeds for the free electrons. Also, the plasma frequency peak in the loss function spectrum for all Ge wetted samples is lower than the same peak of the non-wetted ones or wetted with Ni. This is also caused by seg-
regration, as Ge atoms do not contribute to the plasma frequency of silver. For every sample measured 10 days after deposition, with the exception of the one annealed at 300 °C, where more complicated effects occur, the maximum of the plasma frequency peak in the LF spectrum is blueshifted by 2 nm, which is the same as in the case of silver films deposited on Ni wetting layer. This confirms, that the shift is connected to foreign atoms present at the grain boundaries of the silver film.

The presence of Ge atoms segregated into the grain boundaries results in an additional Lorentz-shaped band in the imaginary part of permittivity, centered within 465–585 nm range for different samples. This band originates from plasmonic resonance of subsurface silver grains, which, surrounded by Ge atoms act like isolated nanoparticles [13]. The position of the peak gives information about the maximum size of those grains, while its intensity gives information about the percentage of grains coated with germanium. As segregation progresses, more grains with greater size become surrounded by Ge atoms. Larger grains have their plasmonic resonance in longer wavelengths and give a more intense response to illumination. That should be observed as the increase and redshift of the peak over time, which has been proven by our measurements – the peak redshifts by 60 nm and increases its maximum by 84% over 50-day period for the non-annealed 20 nm-thick silver film.

In each case, the value of Drude term as well as the maximum of the plasma frequency peak in the loss function spectrum is greater for 35 nm-thick silver films than for 20 nm-thick ones. This is only natural, since the Ge to Ag ratio is smaller in thicker Ag films and therefore germanium atoms have less impact on the effective permittivity of the whole system. Annealing the samples at 100 °C seems to prevent the segregation process – 0° peak and Drude term increase, and the Lorentz-shaped band centered in the middle of the visible range in the imaginary part of permittivity diminishes. However, the XPS measurements suggest something else. Fig. 4d depicts the atomic concentration of Ge atoms in four different samples deposited on Ge wetting layer. Etching time is equivalent of the subsurface depth. Due to the slight thickness inaccuracy of Ge, Ag, and LiF layers (the nominal accuracy of the quartz weight is 5%) as well as varying, trace amounts of adventitious carbon and oxygen on the surface, the curves cannot be compared to one another (hence the arbitrary units on the vertical axis). However, the tendencies are visible and can be discussed. Contrary to the 100 nm silver film fabricated previously [13], where only a fraction of germanium segregated into silver structure over a two-week period, in the case of 20 nm-thick silver films, 10 days is enough for 2 nm of Ge to segregate through the whole thickness of the silver film. The Ge concentration curve for the sample annealed at 100 °C does not differ much from the concentration curve of the non-annealed one – segregation is still observed and is more profound near the surface than in the volume of the Ag films. However, the amount of Ge atoms detected by XPS measurements for 100 °C-annealed, 20 nm-thick LiF-covered sample after a minute of etching is greater than before etching. It suggests, that Ge atoms have lowest energy
in – and thus migrate to – the subsurface grain boundaries rather than the Ag/LiF interface. If we also consider, that in the XPS measurements, the photoelectrons are collected from a few nm depth, it may be possible that Ge atoms detected before etching are not those present on the surface, but also in the close subsurface grain boundaries. The reason for this is that isolated Ag nanoparticles (with large surface) have a lower melting temperature than adjacent Ag nanocrystals of the same size [37]. The same must apply for surface grains (lower melting point) versus subsurface grains (higher melting point). Therefore, surface grains should form bigger nanocrystals than subsurface grains at the same annealing temperature, thus hindering the segregation process. However, the results obtained for the sample annealed at 300 °C suggest another mechanism. The segregation-induced band in the imaginary part of the permittivity for this film is 5.6 times smaller than the one for the non-annaeled sample and has similar intensity as the Lorentz-shaped interband transition peak. This implies that almost no atoms are present in the Ag grain boundaries. The XPS measurements, however, indicate that germanium has segregated into the silver film annealed at 300 °C. Contrary to diffusion, which would cause the least Ge atoms be at the surface and most at the Ag/SiO₂ interface, segregation leads to large amounts of germanium being detected after short etching periods and smaller amounts after greater etching periods. It means that Ge atoms have segregated into the silver film, but have somehow left the grain boundaries.

The inset in Fig. 4d presents the temperature evolution of XPS band of Ge in a non-etched 20 nm-thick silver layer wetted with Ge. This band consists of two Gaussian components even at room temperature, but with the increase of temperature, the taller, lower energy component increases. We conclude that the high energy component from germanium present at the grain boundaries while the low energy component comes from germanium not present at the grain boundaries, possibly forming an alloy with silver. In principle, such alloy formation should prevent any further segregation, but the ellipsometric measurements repeated after 50 days for the 20 nm-thick, Ge-wetted Ag layer annealed at 100 °C show that segregation progresses, which implies that for silver layers annealed at 100 °C, the more likely mechanism is the surface grain growth.

To verify the connection of segregation with surface smoothing-and crystallinity, we have fabricated a sandwich-like film, where 20 nm of silver was deposited directly on SiO₂ substrate, then 2 nm of germanium was deposited on top and covered with another 20 nm of silver. The whole sample was capped with a 3 nm LiF to avoid oxidation. The atomic concentration of germanium in this sample is shown by the orange curve on Fig. 4d. Although Ge atoms may migrate towards two similar interfaces of Ag/SiO₂ at the bottom and Ag/LiF at the top, germanium only segregates towards the Ag/LiF interface. This indicates, that germanium would only segregate in a layer grown on germanium and since segregation is intrinsically connected to crystallinity, Ge wetting layer must influence the crystallinity of the Ag film deposited on top, which results in a smoother surface.

4. Conclusions

We have fabricated plasmonic nanostructures containing 20 and 35 nm-thick silver films deposited either directly on SiO₂ substrates or with the use of Ni and Ge wetting interlayers. Then we have determined the permittivity of the silver layers by ellipsometric measurements. The use of Ni wetting layer allowed for narrowing-and diminishing of the Lorentz-shaped interband transition peak due to the decreased roughness of the silver film, but it also slightly decreased the Drude term. The use of Ge wetting layer has strongly decreased the Drude term and introduced an additional, segregation-induced band in the imaginary part of permittivity. The position and intensity of this band were controlled by time and annealing. We have suggested two mechanisms of annealing-based diminishing of this segregation-induced band: surface grain growth and alloy formation.

Appendix A. Supplementary data

Permittivity values of all investigated films can be found in the Supporting information. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apsusc.2017.01.039.

References


