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Investigation of Optical Transmission in Thin Metal Films

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Abstract

Thin metal films have recently attracted large interest due to their practical application in photo-detectors, solar cells and quantum electronics. It is known that thin films of noble metals such as Au, Ag, and Cu have a maximum optical transmittance in the shorter part of spectrum.

In our work, optical properties of thin metals films deposited by thermal evaporation and low pressure ($1.33 \cdot 10^{-5}$ - $1.33 \cdot 10^{-4}$ Pa) DC plasma sputtering were investigated. Such low pressure is provided by triode sputtering method which supports a ballistic type of mass transfer between the sputtering target and the substrate. This method enables fine control of the film thickness and its density. Comparison of the films deposited by mentioned above two methods on glass substrates shows significant differences in their optical and electrical properties. Thin films of following metals: Sn, Al, V, Ti, Ni, Mo, Ta, W, Au, Ag, and Cu were deposited on glass and their optical and electrical properties were studied. The transmission spectra of thin films of various metals have significant differences. In our paper we discuss the causes of these differences.

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1. Introduction

Thin metal films has attracted large scientific and practical interest since their specific properties enable various applications as transparent conductive coatings for UV spectrum [1], transparent electrodes for “smart windows” and solar cells [2], catalytic coatings for growing ZnO nano-structures [3], active component of surface plasmon resonance (SPR) based biosensors [4] etc. In thin layers, metal films may represent continuous or un-continuous (island) structures. Thin metal films are partially transparent and conductive at the same time. Evidently, the island shape of the metal film increases their transmittance and decreases their conductivity.

As known, conductivity is associated with release of Joule’s heat. This is an irreversible phenomenon, in which the electromagnetic energy is transformed into heat, and in consequence an electromagnetic wave (light) in a conductor is attenuated [5]. In metals, this effect of attenuation is so large that metals are practically opaque. High

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conductivity of metals is due to the high concentration of electrons in them. In metals, a conduction band overlaps with the valence band that creates a metallic type of bonds. Here, the valence electrons play a role of (free) conductivity electrons. By this way, each atom of metal contributes approximately one electron in the common “electron gas” bonding the metal atoms. Therefore, electron concentration will be equal to the atom concentration in metals. However, this claim is correct for a narrow group of metals only: for noble metals and for alkali metals which have only one electron on the outer electron orbit. So, they can contribute this one electron to the conducting band and to build the stable electron configuration like noble gases. Each group of metals behaves differently due to the different number of electrons on outer and next to last electron orbits. So, electronic and optical properties of different groups of metals must be different also.

Strong absorption of light is accompanied with high reflectivity in metals, so that metallic surfaces act as excellent mirrors. Usually, optical properties of metals are studied using experiments with reflection of light. However, interesting and attractive effects may be discovered in thin and extremely thin metal films. In this case, absorption and transmission experiments may take very important information enabling observation and evaluation of material constants of metals and pick out thin effects in metal films.

The most interesting effects are seen in thin metal films with a critical thickness – thickness of transition between continuous and island films. At this thickness, the films appear anomalous optical properties in the near UV and visible light. To define, what the anomalous behavior is, we must to define the normal behavior. Thus, the normal behavior is the behavior obeying the Beer-Lambert's law. Therefore, all deviations from the monotonic changes in the spectral characteristics can be considered as anomalous.

Various deposition methods may be applied to prepare thin metal island film. Thermal evaporation method is simple and enables deposit thin films of noble and transition metals. Main problem in this case is in the adherence of these films and their stability. Also, thin films of refractory metals cannot be evaporated by this way. Sputtering deposition methods provide higher energy to the deposited particles and suitable adherence of the films. However, these methods use working pressures of a relatively high level that influence on the properties of deposited films. While sputtering, gas molecules can be captured by deposited particles and inserted into the growing films. Evidently, that changes thin effects in the films and hide them. If to apply for deposition of thin metal films sputtering at lower pressure, one can get more pure films from high energetic sputtered particles [6]. By this way and using suitable heating of the substrate, a shape and dimensions of the metal islands may be controlled. In this work we describe our research of optical properties of various thin metal films grown by vacuum thermal evaporation and low-pressure plasma sputtering methods.

2. Experimental details.

Thin metal films were deposited using two different deposition systems: a laboratory triode sputtering vacuum station realizing the plane-shape plasma discharge, working at low pressure of $1.33 \cdot 10^{-5} - 6.65 \cdot 10^{-4}$ Pa [6] and a laboratory thermal evaporation vacuum station working at residual pressure of $2.66 - 4 \cdot 10^{-6}$ Pa. Both deposition machines were equipped with the same two-stage vacuum systems based on the diffusion pumps and providing residual pressure of $2.66 - 4 \cdot 10^{-6}$ Pa. The films were deposited on glass substrates cleaned using ultrasound bath in isopropyl alcohol and drained by a compressed air flux. Precisely polished and cleaned using standard RCA technology silicon substrates were used for thickness measurements.

For our experiments, we selected four groups of metals:

1. Noble metals Au, Ag and Cu characterized by fully filled next to last electron orbit (d-shell) and one weakly bound electron.
2. Transition metals Ti, V and Ni, characterized by not filled d-shell.
3. Refractory metals Mo, Ta and W which are transition metals also, however they are very stable at high temperature due to their high atomic weight.
4. Semimetals Al and Sn characterized by fully filled d-shell and several electrons on the last orbit.

Metal films of first, second and fourth groups were deposited by vacuum evaporation at residual pressure from tungsten and molybdenum evaporation cells. During the deposition, substrates were kept at room temperature. Deposition was provided up to full evaporation of material from the cell. Portions of the material for evaporation were prepared with help of the microbalance ViBRA. Value of this mass was found by calculation from the defined film thickness using follows relation written for the point evaporation source [7]:

$$d = \frac{M \cos\theta}{4\pi\rho R^2} \quad (1)$$

Here M is the mass of the evaporated material, ρ is the material density, R is the distance between an evaporation source and a substrate, and θ is the deposition angle defined by geometry of the substrate. Of course, application of this formula for extremely thin films is may be used for evaluation of an average thickness only. In this case, different assumptions about the structure of the film, the shape and size of the islands can only be made on the basis of measurement of electrical and optical properties of this film and topographic surveillance using SEM or AFM.

Evidently, refractory metals cannot be evaporated by resistive evaporation method. To deposit thin films of the third group of metals we applied DC sputtering at the home-made setup realizing the plane-shape low-pressure sputtering [6]. Also, thin films of other groups of metals were deposited by sputtering to compare properties of extremely thin metal films deposited by different methods. Thus, we have deposited thin films of noble metals (Au and Cu), transition metals (Ni and V), and films of semimetal, Sn. These experiments were done using pure metal targets (99.999) of 50 mm in diameter and of 3-6 mm of thick, in an argon atmosphere.

The relatively low operating pressure for the sputtering setup was accomplished by a high concentration of ions in the gap between the target and the substrate. The flat shape of the plasma was achieved using the collimator and external magnetic field. Basic technological parameters of sputtering deposition processes are shown in table 1.

Table 1. Sputtering technological parameters.

Parameter	Designation	Value	Units
Argon pressure	P	$(1.33 - 66.5) \cdot 10^{-5}$	Pa
Substrate temperature	T _S	50 - 250	°C
Magnetic field strength	H	120-140	Oe
Sputtering voltage	V _T	800 – 2000	V
Ion current	I _T	20 – 30	mA

Thickness of thin films deposited by sputtering was defined by the deposition duration due to a high stability of the sputtering process. To define a deposition rate while sputtering, relatively thick films (more than 100 nm) were deposited on silicon substrates with the step shape. The height of the step (thickness of the film) was measured using a home-made computerized micro-interferometer [8].

A standard four-point probe method was applied to measure the sheet resistance of the deposited metal films. The surface structure was studied using the SPM DI300 in AFM contact mode and the computerized metallurgical microscope “Nicon-Optiphot 100” with optical magnification of up to $\times 1600$. Optical absorption and transmittance of metal films were measured at wavelengths of 200-1100 nm using the UV-2800 UV/VIS spectrophotometer of UNICO.

3. Results and discussions.

Bulk metals are opaque for the light. This is due to the high concentration of free charged carriers in the metals. However, in thin films, metals begin behave in a different way. Their electrical and optical properties begin to depend on the frequency of the incident electromagnetic wave (light). These films are beginning to be transparent and take on some new properties such as increased transparency at certain frequencies [9] or frequency of extremal absorption dependence on the size and shape of the islands in case of extremely thin metal films [10]. Generally, an electromagnetic wave incident on metal interacts with it by help the mechanisms of absorption. However, some energy can pass through thin layers of metals. This part ensures the transparency of metals. Dominating absorption mechanisms of light in metals may be presented by two various contributions of electrons: intraband optical processes and interband optical processes. In intraband processes, electrons and holes belonging to the same energy band. These processes can be described in first approximation by a Drude dielectric function. The interband processes relate to transition of electrons and holes from band to band. These processes correspond with the Lindhard dielectric function taking into account the Coulomb interactions, the electron-phonon interactions and the

electron scattering at interfaces [11]. Superposition of these two mechanisms defines features of a dielectric function of metals in the visible and near UV range.

According to the Beer-Lambert's law, the intensity of light in absorbing media decreases exponentially as seen from the following equation:

$$I = I_0(1 - R) \exp(-\alpha x) \quad (2)$$

Where I_0 is the intensity of the incident light, R is the reflectance, x is the thickness of the film, and α is the absorption coefficient defined by follows way:

$$\alpha = \frac{4\pi\kappa}{\lambda} = \frac{2\pi\epsilon_2}{\lambda n} = \frac{\sigma}{nc\epsilon_0} = \frac{2\omega\kappa}{c} \quad (3)$$

Where κ is the extinction coefficient responsible for the photons absorption, λ is the wavelength of incident photons, n is the refraction coefficient of the media, ϵ_2 is the imaginary part of a complex permittivity of the media, ϵ_0 is the permittivity of vacuum, c is the light velocity, σ is the conductivity of media, and ω is the circular frequency of the light. According to the energy conservation law, absorption with reflectance and transmittance constitute the total energy of an incident light:

$$I_0 = I_R + I_T + I_A \quad (4)$$

Where I_R is responsible to the reflectance, I_A is responsible to the absorbance, and I_T characterizes the transmittance. So, if the spectral absorption and transmission characteristics will behave according to equations (2) and (4), we can say that it is the normal behavior. However, if the measured spectrum shows some features different from expected monotonous variation, we see the anomalous behavior which requires explanation and application.

Thin films of noble metals are of particular interest because of their stability and reproducibility. Usually, these films are prepared by thermal evaporation in vacuum due to simplicity and affordability of the process. Main drawback of this process is the low adhesion of films due to the low energy of evaporated particles. Figure 1 presents transmittance characteristics of very thin films noble metals. !

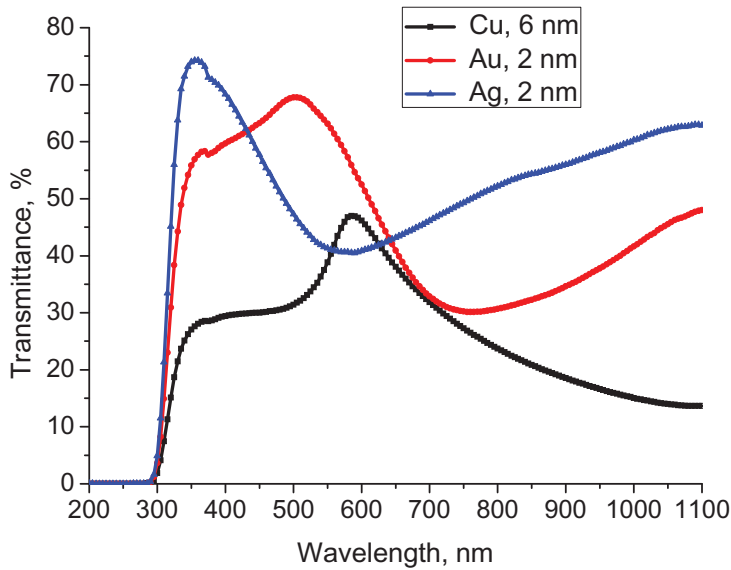


Fig. 1. Transmittance of very thin noble metals films.

As shown, thin films of these metals are transparent at thickness of 2-6 nm and their characteristics do not look monotonous. They have a maximum in the visible range depends only on the type of material. The absorption edge at 300 nm for all materials is due to absorption of the glass substrate. Thin Ag films have this maximum at $\lambda \approx 350$ nm, thin Au films have the maximum at $\lambda \approx 500$ nm and Cu thin films have the maximum at $\lambda \approx 600$ nm. This maximum has a constant place in the spectrum and is not dependent on the film thickness. This is illustrated by figure 2.

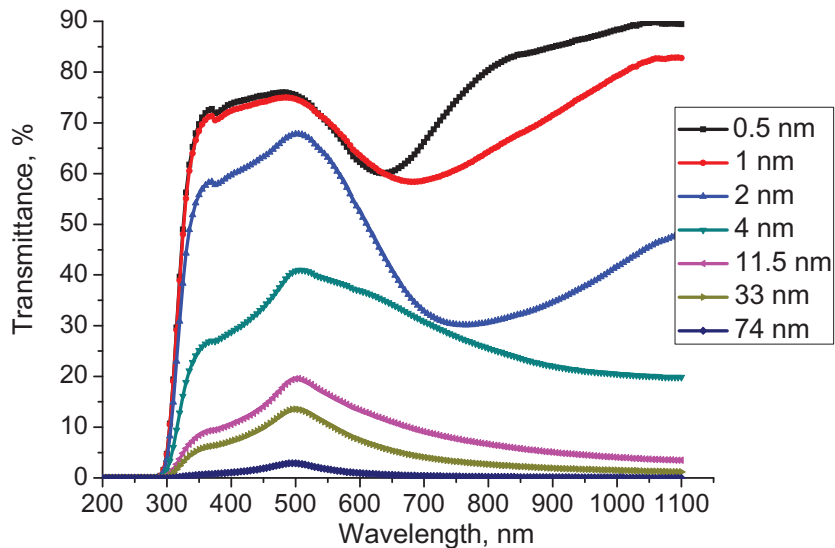


Fig. 2. Transmittance of thin gold films deposited by thermal evaporation.

All thin films of gold deposited by thermal evaporation method have a transmittance maximum at $\lambda \approx 500$ nm, however at longer wavelength they behave differently. One can see that more thin films have a transmittance

minimum which depends on the film's thickness. Moreover, the location of this minimum is associated with the film thickness and disappears at the transition to a continuous film. Thus, we see two different types of anomalies inherent in the gold films: a constant maximum, depending on the nature of metal and the least variable associated with structure of the film. Obviously, these two phenomena have different explanations.

The metals having fully filled d-shells, the noble metals, enable the interband transition of photons only. Therefore, the maxima of transmission spectra for such metals are conditioned by existence of bulk absorption modes according to their dispersion equation $\omega = \pi c / \sqrt{\epsilon_2(\omega)}$. So, these maxima at $\lambda = 570$ nm for Cu, 500 nm for Au, and 320 nm for Ag are revealed as for island as for continuous flat films [12]. This explains the yellow light of gold and reddish light of copper.

The nature of these minima shown in figure 2 can be explained by appearance of localized plasmons with the intensity and frequency relative to the size of the islands of the film. The absorption spectrum of thin gold films prepared by evaporation method with thickness calculated using formula 1 is shown in figure 3.

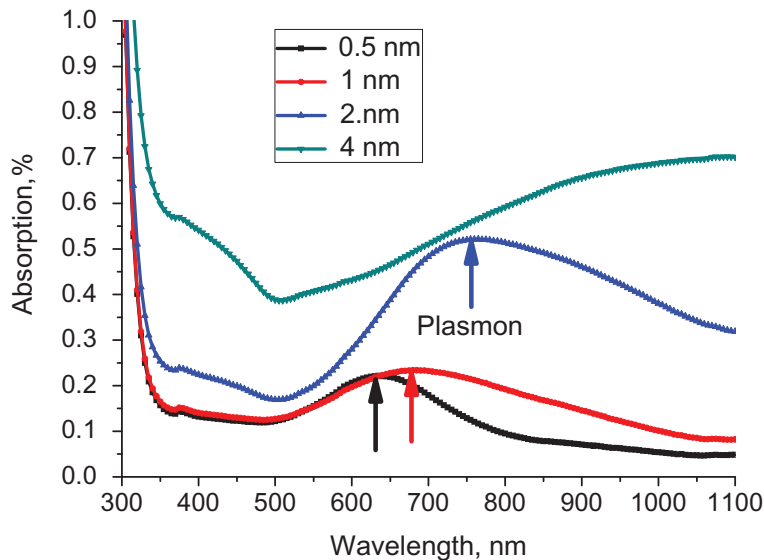


Fig. 3. Plasmon appearance in the absorption spectrum of gold films.

The localized surface plasmons represent collective behavior of free electrons confined to the gold particles. In other words, surface plasmons are coherent fluctuations in electron density occurring at a "free-electron" metal-dielectric or metal-air interface. Mie theory and Maxwell-Garnet theory explained the surface plasmon resonance (SOR) in terms of higher moment oscillation and particle size [13-14]. Although, it has been found that the width and peak position of the SPR are depends on the particle size, shape and environment [15]. In accordance with the size of these nano-particles, as shown in figure 3, the plasmon is shifted in frequency with the growth of these particles. The measured spectrum shown in figure 3 looks like the absorption spectrum for a thin film of gold nano-particles embedded within an organic dielectric with permittivity $\epsilon_d \approx 2.5$. The particle size was of 6-7 nm [16]. The main difference in our results is that the role of an insulator in our experiments was gained by ambient air.

Figure 4 represents AFM 3D-topographic evaluation of the extra-thin gold films grown by thermal evaporation on glass substrates: 4a - 0.5 nm, 4b - 2 nm and 4c - 4 nm of average thickness. According to these pictures, tentative estimation of the gold islands dimensions in the equal surfaces of 100×100 nm was done. The results are presented in table 2.

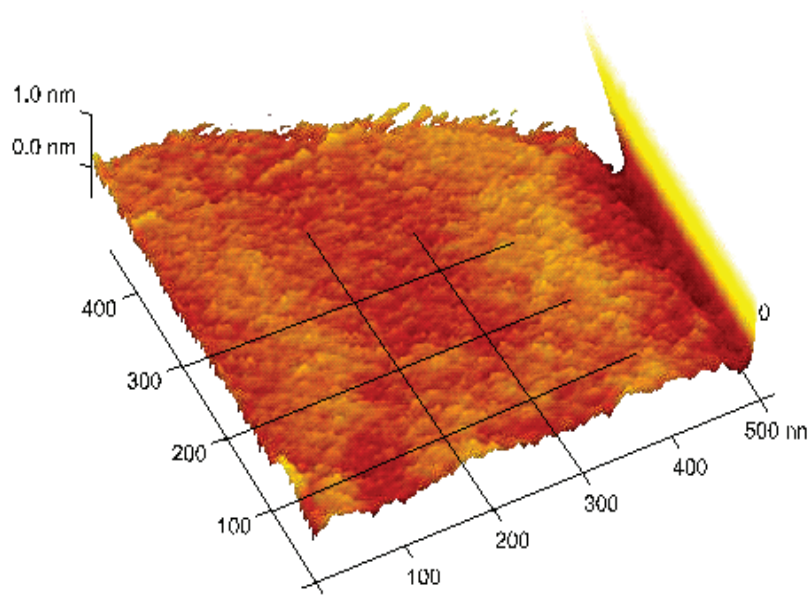


Fig. 4a. Gold film of 0.5 nm thick on the glass substrate.

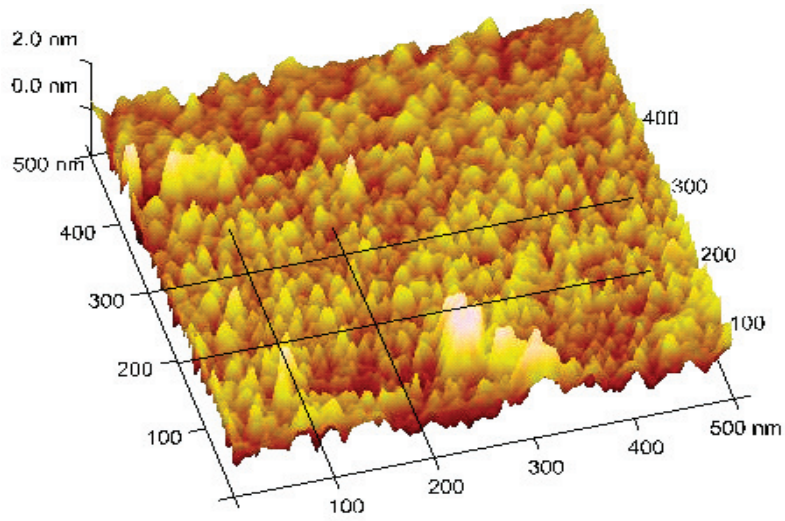


Fig. 4b. Gold film of 2 nm thick on the glass substrate.

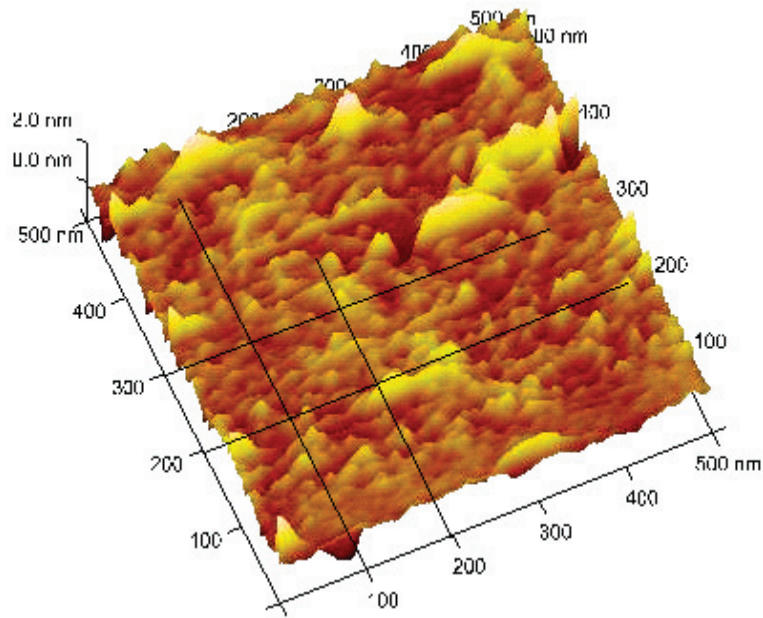


Fig. 4c. Gold film of 4 nm thick on the glass substrate.

Table 2. Estimated parameters of gold island thin films.

Calculated thickness, nm	Number of islands	Height of islands, nm	Dimensions, nm
0.5	27-30	0.2	10
2	27-30	1	14
4	27-30	1.5	20

As shown, the number of islands does not depend on the film thickness. The area of the islands depends on the film thickness or of the amount of deposited material. Such type of growth or 3D growth is described by the Volmer-Weber's model [17]. Many metals grow in accordance with this model. The main reason for this type of growth is that the binding energy of atoms within the cluster exceeds the binding energy of the metal atoms with the substrate surface. Figure 5 illustrates the Volmer-Weber's model.

Coverage Mechanism	$\theta < 1 \text{ ML}$	$1 < \theta < 2 \text{ ML}$	$\theta > 2 \text{ ML}$	Examples
3D island growth				Metals on SiO_2

Fig. 5. Model of Volmer-Weber for thin films growth [17].

It is of interest to compare extremely thin gold films deposited by evaporation and by sputtering. Figure 6 presents transmittance characteristics of such films.

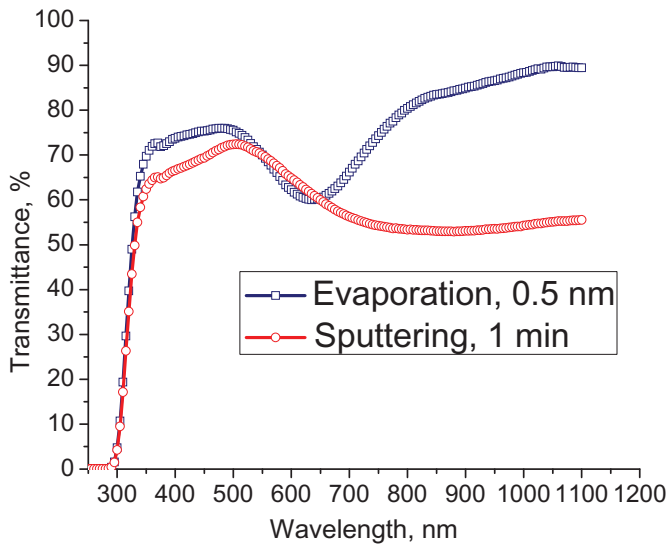


Fig. 6. Transmittance of extremely thin gold films prepared by various methods.

The characteristics presented in figure 6 show that the films prepared by sputtering are denser than films deposited by evaporation. Despite the fact that the films have approximately the same thickness, a plasmon appeared by the sputtered film is broader and its absorption peak is shifted to lower energies. Thin films of other noble metals behave like gold films. This is confirmed by figure 7 which presents estimated extinction coefficient for extremely thin films of Au, Ag, and Cu.

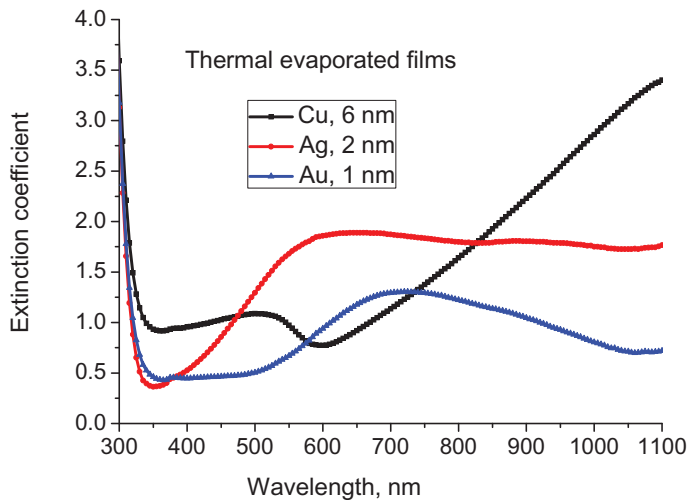


Fig. 7. Extinction coefficient of the noble metal films.

Calculation of the extinction coefficient was done using measured absorption spectrum via equation (3):

$$\kappa = \frac{\alpha d}{4\pi} \quad (5)$$

where α is the measured absorption. Characteristics presented in this figure show absorption maxima for each film due to the plasmon appearance.

Thin films of transition metals behave differently from noble metals. Figure 8 represents transmittance characteristics of transition metals.

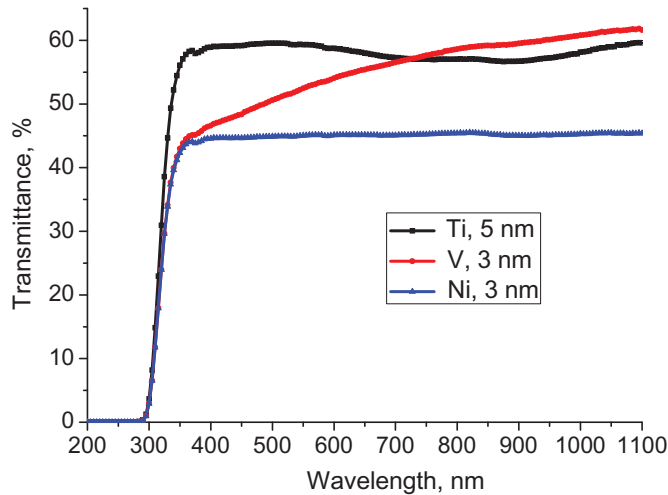


Fig. 8. Transmittance characteristics of extremely thin films of transition metals.

Transmittance of these films is practically constant at visual range or increases monotonically. These films behave as grey filters without features which may attract any attention. In order to check on a possibility to build surface plasmons, the absorption characteristic was measured for thin films of transition metals. These characteristics are presented in figure 9.

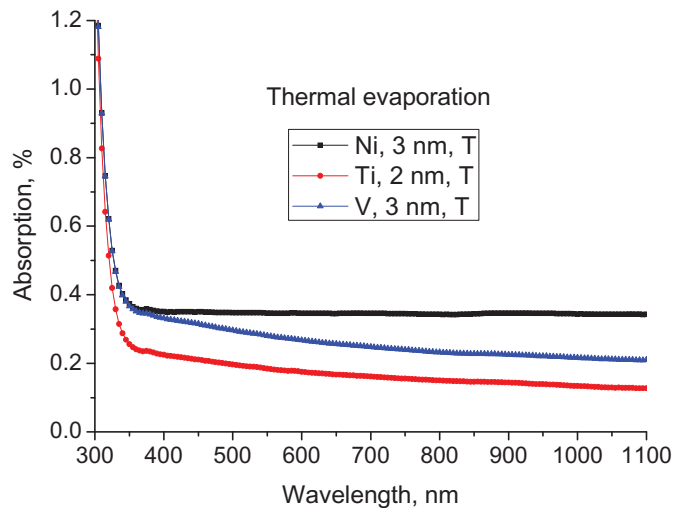


Fig. 9. Absorption characteristics of transition metals.

As shown, absorption spectra of these films have no spectral features as well.

Such materials as refractory metals are transition metals also. The main difference is due to high melting point of these metals. So, the absorption characteristics of such metals as Ta, Mo and W looks like to the characteristics of

usual transition metals such as Ti, Ni, and V. Electron structure of these metals provides for them other attractive properties: they can be oxidized in different ratios with oxygen. This leads to the so-called “smart” oxides that change their crystal structure under the influence of external factors such as temperature, electric fields etc. Absorption characteristics of refractory metals are shown in figure 10.

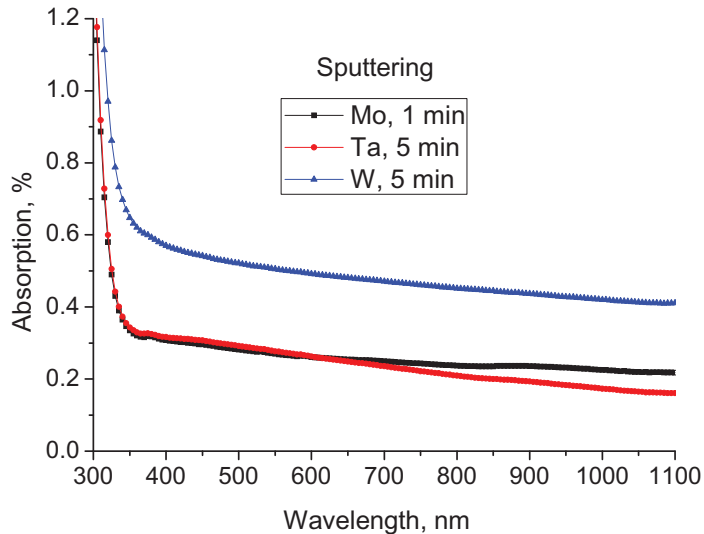


Fig. 10. Absorption characteristics of refractory metals.

A “normal” behavior of all transition metals may be explained by not full d-shell in their electron structure. In these metals, the intraband transition of electrons under irradiation prevails due to the existence of free states in the valence band. Their plasma frequency shifts in the high energy region which leads to the low transmittance and absorption in the visible and near ultra-violet range.

Transmittance characteristics of extremely thin films of Al and Sn which represent a group of semimetals (or “other” metals [18]) are presented in figure 11.

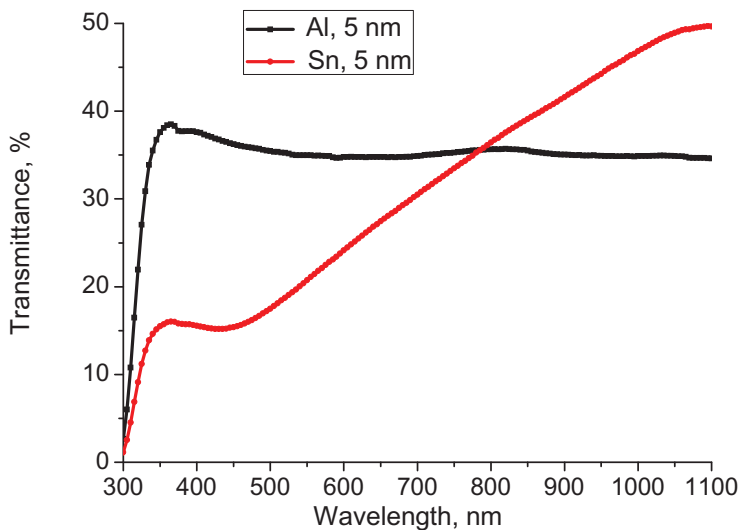


Fig. 11. Transmittance characteristics of semimetals.

A distinctive feature of this group of materials is completely filled upper d-shell of the electron structure. However, in contrast with noble metals these materials have more than one electron at the upper level: s- and p-electrons. All these electrons can participate in the conduction and transfer energy into heat. When the photons with sufficient energy (greater than the plasma frequency) will reach the surface, the absorption of external energy due to interband transitions will dominate. In the case of nano-particle materials, there will be localized plasmons with the magnitude and frequency determined by the size and shape of nano-particles. Figure 12 presents absorption spectrum for two semimetals, Al and Sn.

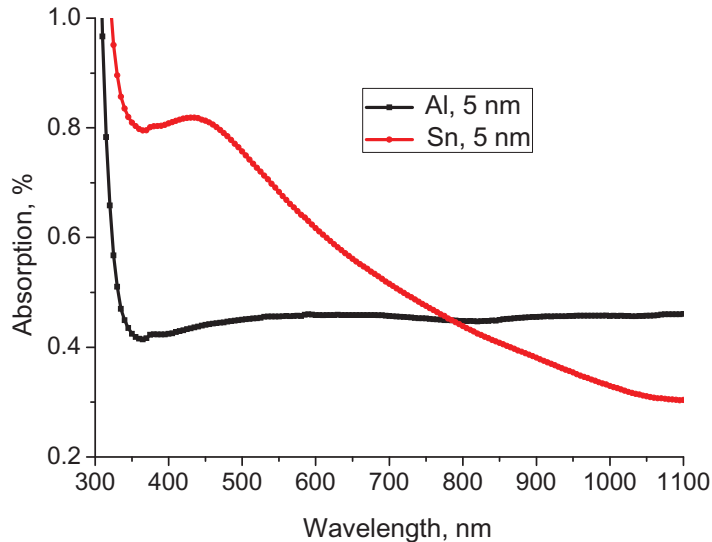


Fig. 12. Absorption characteristics of semimetals.

These films behave like to the noble metal films. One can see that these films have maximum absorption in the visual or near ultra-violet range. It is interesting to note that films prepared by sputtering behave like to noble metals too. They are denser and their particles are smaller with the approximately same thickness. Both methods: evaporation and sputtering may be used for these films preparation. However, more intense effects are obtained in the case of lower-energy particles, i.e. in the case of thermal evaporation in vacuum.

To be useful for surface plasmon resonance, metal must have conduction band electrons capable of resonating with light at a suitable wavelength. The visible, near ultra-violet and near infra-red ranges of the spectrum are convenient for this, depending on the expected application: photo-voltaic cells, optical components or high performance detectors. There are many metals satisfying these conditions. They include silver, gold, copper, aluminum, sodium, indium [19]. The specific application imposes additional requirements, such as resistance to oxidation and other chemical reactions. Because of these additional requirements, researchers pay maximum attention to the noble metals [20-22]. However, these materials may also be applicable if they are embedded into dielectric matrix or coated by a dielectric protective coating. It should also be noted that according to our experiments, only metals or semimetals with a completely filled d-shell can be used to create items based on the surface plasmon resonance.

4. Conclusions

Optical characteristics of four group extremely thin films of metals were studied in this work. They were noble metals, transition and refraction metals and semimetals. Thin films were deposited by vacuum evaporation and by DC plasma sputtering at relatively low pressure. Sputtering was realized using home-made setup providing an original method of sputtering with sheet-shaped plasma. For all 11 different metals (Ag, Au, Cu, Ti, Ni, V, Mo, Ta, W, Al, Sn), thin films of various thickness were prepared.

Absorption and transmission characteristics and sheet resistance were measured for all thin films. Analysis of these characteristics showed the following:

1. Thin films of noble metals grow on the glass substrates according to the Volmer-Weber's model;
2. Thin films of noble metals and semimetals show appearance of surface plasmon resonance at low thickness island's films.
3. Intensity, width and frequency of plasmons depend by size and shape of the islands making up the film;
4. The deposition method influences the plasmons appearance and their shape, films deposited by sputtering have wider plasmons with frequency shifted in the region of lower energies;
5. Thin films of transition metals and refraction metals do not show features as thin films of noble metals;
6. Thin films of metals having completely filled d-shell can only produce plasmons. These metals are: alkali metals, alkaline earth metals, noble metals and semimetals.

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