Adsorption Effect on the Successive Ionic Layer Adsorption and Reaction Technique

A. Abderrahmane[a,b], M. Kaddouri[c], M. Adnane[c], S. Hamzaoui[a]

[a]Laboratory of Electron Microscopy and Materials Sciences,
University of Sciences and Technology of Oran,
P.O. Box 1505, 31000, El-Mnaouer, Oran, Algeria,
e-mail: abderrahmane.abdelkader@gmail.com
[b]Department of Energetic Physics,
University of Sciences and Technology of Oran-Mohammed Boudiaf (USTOMB), Oran, Algeria
[c]Laboratory of Analysis and Applications of Radiation,
Department of Physics Engineering, Faculty of Physics, University USTOMB,
P.O. Box 1505, Oran, 31036, Algeria

We carried out a series of experiments of metal sulfide deposition on glass and copper substrates by the successive ionic layer adsorption and reaction (SILAR) technique. This technique based on the cations adsorption process involves the presence of the van der Waals and electrostatic forces. According to the theoretical study discussed herein, the equilibrium separation between cations and the substrate surface was lower in the case of a copper substrate than that of a glass one confirming the observed experiments results obtained by the SILAR technique. The surface charge of the glass substrate is strongly dependent on the solution pH. In the absence of the surface charge, the dominant forces between cations in solution and the glass substrate were repulsive in contrast with the case of the copper substrate in which attractive forces dominate even if the surface is somewhat positively charged. This study enriches the knowledge on the optimization parameters for fabricating thin films of metal chalcogenide of good adherence.

Keywords: *thin films, successive ionic layer adsorption and reaction, adsorption, metal chalcogenides, van der Waals forces, electrostatic forces.*

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INTRODUCTION

Thin films are widely used in electronic semiconductor devices and optical coatings. The chemical techniques used for thin films deposition, unlike physical techniques, are inexpensive, however, the thin films obtained are of poor quality compared with those obtained by physical methods. The successive ionic layer adsorption and reaction (SILAR) method, one of the newest techniques for the thin films deposition, is low-cost, low-temperature, and eco-friendly, where neither sophistical equipment nor a high vacuum chamber are needed. SILAR proceeds via a layer-by-layer fabrication of a thin film, somewhat analogous to a molecular beam epitaxy [1]. In addition, SILAR is a promising technique for deposition of two-dimensional (2D) materials such as MoS_2, $MoSe_2$, WS_2, etc., and their combinations – materials which recently have been attracting high interest due to their exotic electronic and optoelectronic properties [2–6].

The SILAR technique is based on the cations adsorption from a cationic solution on the substrate surface by physical forces. The substrate immersed in an electrolyte solution acquires a surface charge due either to chemical dissociation of surface groups or to adsorption or desorption of ions. Ions involved in the mechanism of surface ionization are called potential-determining ions (PDI). In the case of a metal oxide substrate, hydronium ions (H_3O^+) are the PDI [7] and the protonation or deprotonation generate a surface charge, consequently, the surface charge highly depends on the pH of the electrolyte solution.

Quite a lot of researchers are focusing on the study of SILAR deposition parameters such as the effect of the rinsing steps, the immersion cycles, the solution concentration, etc.[8–10]. In this paper, we offer certain experimental results of some metal sulfide deposited on glass and copper substrates. We discuss the adsorption effect on the thin films formation and adherence basing on the interaction model proposed by Malysheva, Tang, and Schiavone [11]. Only at cationic solution with pH higher than 3.5, the interaction is attractive on a glass substrate, whereas the equilibrium separation between cations and the glass surface increased with decreasing the pH of the cationic solution and the interaction energy increased, which means poor adherence of a thin film to the substrate. In case of a very acidic cationic solution, the repulsion forces between cations and the glass substrate surface dominate. The cations adsorption occurs on the copper substrate either in the absence of a substrate surface charge or when it is slightly positively charged.

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EXPERIMENTAL

Principle and technique automation

The SILAR technique is based on the successive immersion of the substrate: first, in a cationic solution, washed in distilled water to remove the poorly-adsorbed cations, then in an anionic solution in which the anions react with the pre-adsorbed cations at the substrate surface forming the desired compound semiconductor and finally in distilled water to remove the loosely-reacted particles. These four steps represent one cycle whereby only a monolayer can be formed with a typical thickness of 1–3Å [12]. This cycle is repeated many times in order to obtain the desired thickness of the thin film. Figure 1a depicts schematically the four steps of the SILAR technique.

Roughly speaking, deposition of a thin film of the thickness of a few micrometers requires hundreds of cycles and therefore the automation would be useful. Figure 1b shows a microcontroller-based automatic system used to elaborate thin films of a metal sulfide.

Substrate cleaning

Cleaning of the substrate is an important parameter in the SILAR technique since no additional forces, such as electric or thermal heating energies, intervene to enhance the deposition and the adhesion of thin films. In order to achieve good adhesion of cations on a substrate, the surface must be hydrophilic. Here, we used a glass micro-slides substrate (75×25×1 mm). We used the following cleaning process: the substrates were immersed in 20% HCl solution, and then ultrasonically cleaned in beakers: one containing distilled water and the other – a mixture of ethanol: acetone 1:1 and distilled water. It should be noted that each immersion has been carried out during 20 min in each beaker. Finally, the substrates were dried in a nitrogen gas flux. A copper foil of 25 μm thickness with a purity of 99.8% was used as typical metal substrate.

Metal sulfide deposition parameters

Thiourea was used as anionic precursor; it dissolves in an alkaline solution according to the following chemical reaction:

$$CS(NH_2)_2 + 2OH^- \rightleftharpoons S^{2-} + CH_2N_2 + 2H_2O, \quad (1)$$

The Table summarizes deposition parameters of some elaborated metal chalcogenides. All cationic solutions were prepared using distilled water without adding a complexant. The pH values of cationic solutions were not adjusted but the values shown in the Table were due to the hydrolysis of metal ions in water [13]. We observed the morphology of the metal sulfides elaborated using S2500C scanning electron microscope.

RESULTS AND DISCUSSION

Metal sulfides deposition

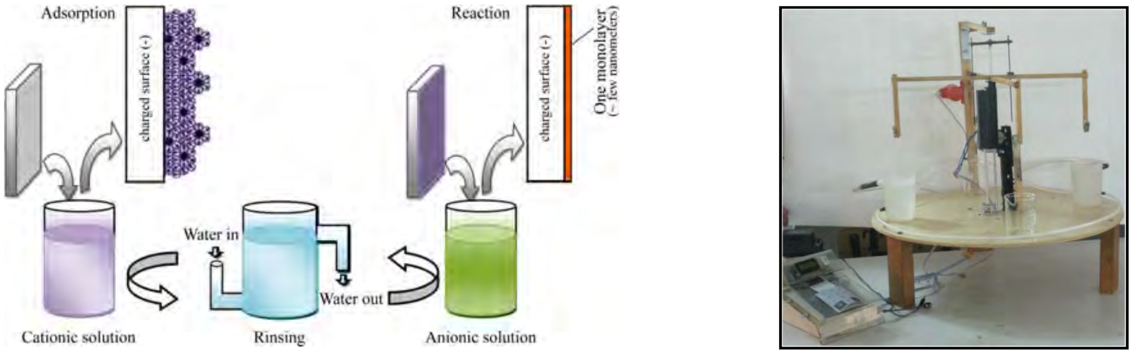
Figure 2a shows a thin film of copper sulfide (Cu_xS) deposited by SILAR on a glass substrate; the value of the optical gap of Cu_xS was about 1.62 eV, a value that belongs to the theoretical value range [10]. Figure 2b represents a 5K magnification SEM image of the formed thin film. Some clusters on the surface were formed due to poor cleaning steps. Figure 3a shows a thin film of silver sulfide (Ag_2S) with different cycle numbers, the growth rate of Ag_2S is about 10 nm per cycle according to Kakade, Nikam, and Gosavi [9]. The thin films were homogenous and uniform. Figure 3b depicts a SEM image of a thin film of Ag_2S annealed in air at 350°C, showing the nanocrystals of Ag_2S.

Figure 4 shows a zinc sulphide (ZnS) thin film deposited by SILAR. After a few cycles, a thin golden-yellow film was formed that became bright-purple metallic with increased thickness. The same was reported by Gao, Li, and Yu [14]. Figure 5a shows a thin film of copper indium disulfide ($CuInS_2$). The concentrations of copper (II) chloride dihydrate ($CuCl_2 \cdot 2H_2O$) and indium (III) chloride tetrahydrate ($InCl_3 \cdot 4H_2O$) were chosen in such a way that the [Cu]/[In] was equal to 1.25, this value showed stoichiometric composition [15]. Figure 5b presents the top view of a SEM image of a thin film where two phases were observed: a bright phase corresponding to In_2S_3 and a dark one corresponding to CuS. Figure 5c is a side view showing the thickness of the studied thin films. The physical properties of each metal chalcogenide elaborated here and resumed in the Table will be discussed in detail elsewhere.

Peeling of the thin films was observed in the case of a glass substrate as shown in Fig. 2a and Fig. 3a, but not in the case of a copper substrate. In other words, in the case of a copper substrate, thin films were more adherent and homogenous. In addition, with the same $CuInS_2$ deposition parameters shown in the Table, i.e. pH of the cationic solution around 3, the thin film formation did not occur on a glass substrate but only on a copper substrate. Thereafter, the pH dependence of the cations adsorption on the glass substrate will be discussed.

Surface Ionization

In aqueous solution, the glass substrate acquires a surface charge due to its surface groups at which a proton H^+ can be acquired, giving a positive charged



(a) (b)

Fig. 1. The SILAR technique scheme showing adsorption, rinsing and reaction steps (a). Mechanism used in the SILAR technique (b).

Table 1. Metal sulphides deposition parameters.

Compound	Precursors		Adsorption time (s)	Reaction time (s)	Rinsing time (s)	Cycles	pH
	Cationic solution	Anionic solution					
Cu_xS	0,025M $CuCl_2 \cdot 2H_2O$	0,05M $CS(NH_2)_2$ + 0,1M NaOH	40	40	40	100–300	~ 4.5
Ag_2S	0,005M $AgNO_3$	0,05M $CS(NH_2)_2$ + 0,1M NaOH	40	40	40	40–50	~ 7
			20	20	30	118	
ZnS	0.02M $Zn(CH_3COO)_2 \cdot 2H_2O$	0,05M $CS(NH_2)_2$ + 0,1M NaOH	40	40	40	120	~ 6
$CuInS_2$	0,01M $CuCl_2 \cdot 2H_2O$ + 0,008M $InCl_3 \cdot 4H_2O$	0,05M $CS(NH_2)_2$ + 0,1M NaOH	40	40	60	195	~ 3

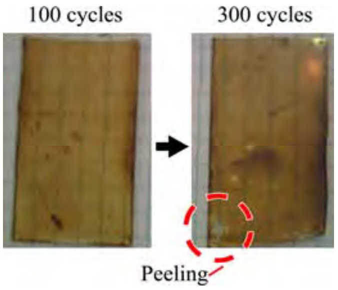


Fig. 2(a). Samples of Cu_xS deposited by SILAR on glass substrate.

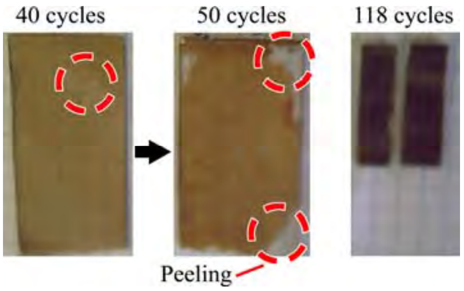


Fig. 3(a). Samples of Ag_2S deposited by SILAR on glass substrate.

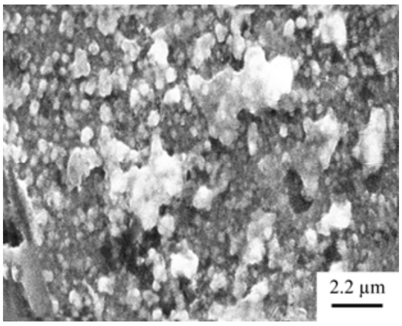


Fig. 2(b). SEM image of 240 cycles of Cu_xS deposited by SILAR on glass substrate, magnification of 5K.

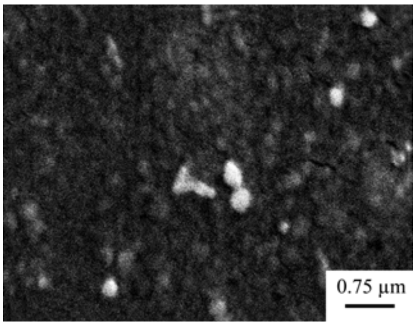


Fig. 3(b). SEM image of 118 cycles of Ag_2S deposited by SILAR on glass substrate annealed at 350°C, magnification of 20K.

surface, or released, giving a negative charged surface, depending on the solution pH. The point of zero charge (PZC) is the pH value at which the surface charge is equal to zero, this value is around 3 in the case of a glass substrate [16]. The silanol groups at the glass substrate surface dissociate according to the chemical reaction [17]:

$$SiOH_2^+ - H^+ \rightleftharpoons SiOH \rightleftharpoons SiO^- + H^+. \quad (2)$$

The glass surface is charged positively at an extremely acidic solution and negatively – when the solution pH exceeds 3. Assuming that the glass substrate surface is a Nernstian surface, then the surface charge density is given by $\sigma \approx -(2.303 C_0 k_B T / q)\Delta pH$ where C_0 is the total capacitance at zero charge, ΔpH is given by the difference (pH – *pzc*), k_B is the Boltzmann constant, is the solution temperature and is the electron elementary charge. The capacity value in the case of SiO_2 is approximately equal to 88.4 µF/cm^2 [7].

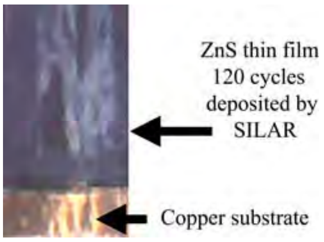


Fig. 4. Sample of ZnS deposited by SILAR on copper substrate.

Fig. 5(a). Sample of $CuInS_2$ deposited by SILAR on copper substrate.

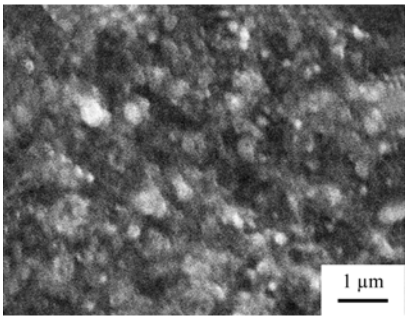


Fig. 5(b). Top view SEM image of 195 cycles of non-annealed thin film of $CuInS_2$ deposited by SILAR on copper substrate, magnification of 11K.

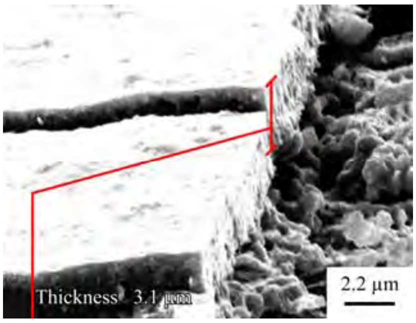


Fig. 5(c). Side view SEM image of $CuInS_2$ deposited by SILAR on copper substrate showing the thin film thickness, magnification of 5K.

Adhesion between substrate surface and charged particle in solution

The adsorption is a surface phenomenon in which ions, or more generally particles, are attracted to the surface by either physical or chemical forces or both. The free energy between a particle in solution and a charged substrate is the sum of the electrostatic free energy measured from the electric potential created by the particle-wall interaction and the van der Waals energy according to the model proposed in [11]. In this model, the effects of the Brownian motion, the hydrodynamic fluid flow, and gravity are ignored.

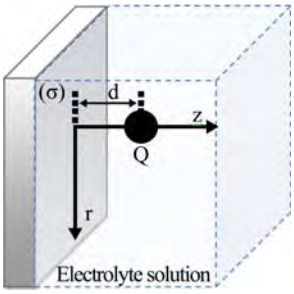


Fig. 6. A particle of charge Q in electrolyte solution near a substrate of initially uniform surface charge density σ.

Let's assume a cation of charge $Q = n{\cdot}q$ is located at distance from a substrate of the surface charge density σ, as shown in Fig. 6, where is the total charge number of the particle. The total dimensionless free energy as given in [11] is:

For metal substrate:

$$g=-\frac{n^2e^{-2\bar{k}_1\bar{d}}}{2\bar{d}}+\frac{n\bar{\sigma}e^{-\bar{k}_1\bar{d}}}{\bar{k}_1}+\frac{8\pi Nc\rho_1 I_B^3}{k_BT}\left[\frac{\bar{r}_0^{12}}{90}\left(\frac{1}{\bar{d}^9}-\frac{1}{\left(\bar{d}+\bar{L}\right)^9}\right)-\frac{\bar{r}_0^{6}}{12}\left(\frac{1}{\bar{d}^3}-\frac{1}{\left(\bar{d}+\bar{L}\right)^3}\right)\right], \tag{3}$$

and for dielectric substrate:

$$g=\frac{n^2}{2\bar{d}}\left[-e^{-2\bar{k}_1\bar{d}}+4\int_0^\infty\frac{\bar{\rho}e^{-2\sqrt{\bar{\rho}^2+\left(\bar{k}_1\bar{d}\right)^2}}d\bar{\rho}}{\varepsilon_{2/1}\bar{\rho}\frac{1+e^{-2\bar{\rho}\bar{L}/\bar{d}}}{1-e^{-2\bar{\rho}\bar{L}/\bar{d}}}+\sqrt{\bar{\rho}^2+\left(\bar{k}_1\bar{d}\right)^2}}\right]+ +\frac{n\bar{\sigma}e^{-\bar{k}_1\bar{d}}\bar{L}}{\bar{k}_1\bar{L}+\varepsilon_{2/1}}+\frac{8\pi Nc\rho_1 I_B^3}{k_BT}\left[\frac{\bar{r}_0^{12}}{90}\left(\frac{1}{\bar{d}^9}-\frac{1}{\left(\bar{d}+\bar{L}\right)^9}\right)-\frac{\bar{r}_0^{6}}{12}\left(\frac{1}{\bar{d}^3}-\frac{1}{\left(\bar{d}+\bar{L}\right)^3}\right)\right]. \tag{4}$$

where $\bar{k}_1^{-1}=1/k_1I_B$, $\bar{d}=d/I_B$, $\bar{\sigma}=4\pi\sigma I_B^2/q$ and $\bar{L}=L/I_B$, are the normalized quantities of the Debye length, the particle-substrate distance, the surface charge density, and the substrate thickness, respectively. These quantities are introduced to simplify the formalizm of the free energy. The quantity $\bar{\rho}$ in Eq. (4) is defined by $\bar{\rho}=\rho\cdot d$. The term $\varepsilon_{2/1} = \varepsilon_2/\varepsilon_1$ is the ratio of the permittivity of the dielectric substrate on the dielectric constant of the solution; $\varepsilon_1 = 80$ and $\varepsilon_2 = 5.75$ are taken as in [18]. N is the atoms number of a particle in the solution and ρ_1 is the atom number density in the substrate. The densities of the copper and the silicone dioxide are 8.96 and 2.27 g/cm^3, respectively, while researchers in [19–20] give atomic densities of 0.085 atoms/Å^3 and 0.023 atoms/Å^3, respectively. The last terms in eq. (3) and (4) correspond to the van der Waals energy represented by the Lennard-Jones formalism. The distance r_0 corresponds to the minimum van der Waals energy and and it is in the order of Å; therefore the normalized distance $\bar{r}_0$ is equal to 0.1429. The symbol is the energy well depth that corresponds to the detached state, the value of c is in the order of 10^{-22} to 10^{-20} [11]. The energy well

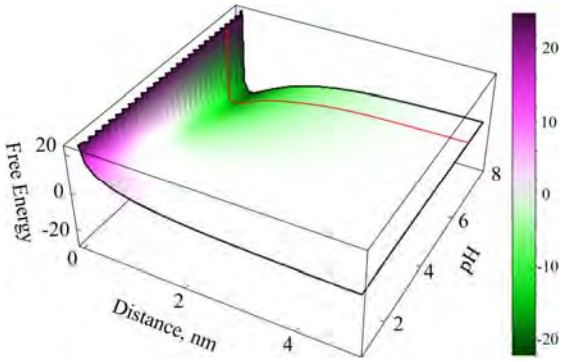


Fig. 7(a). Distance and pH dependence of the normalized free energy of the cations Cu^{2+} near a glass substrate.

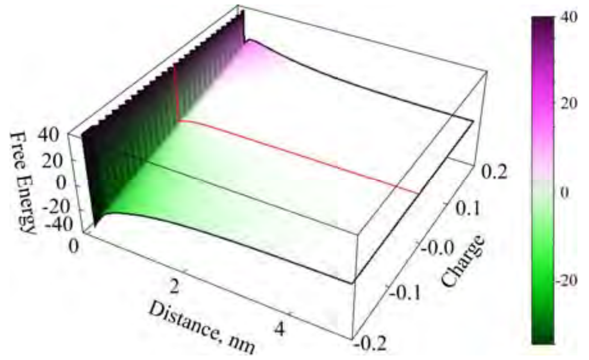


Fig. 7(b). Distance and surface charge dependence of the normalized free energy of the cations Cu^{2+} near a copper substrate.

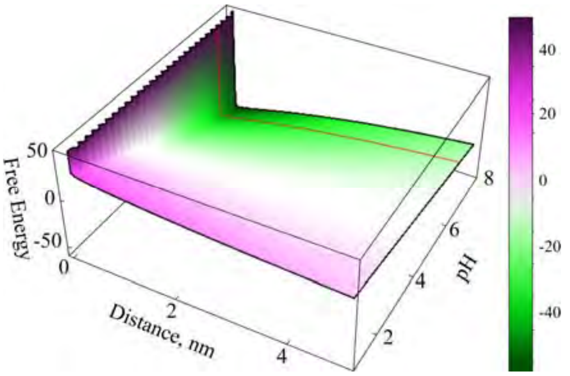


Fig. 8(a). Distance and pH dependence of the normalized free energy of the cations Ag^{+} near a glass substrate.

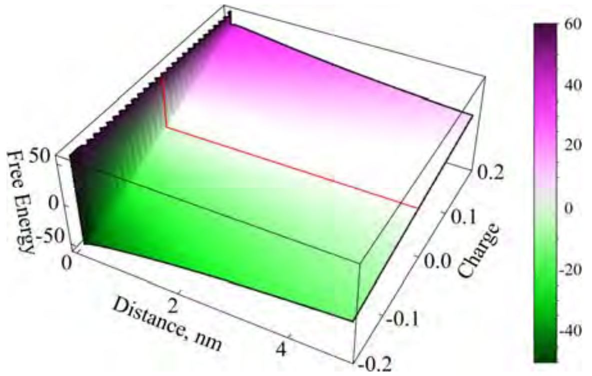


Fig. 8(b). Distance and surface charge dependence of the normalized free energy of the cations Ag^{+} near a copper substrate.

depth was considered to be constant and equal to $2.79 \cdot 10^{-21}$ J [21].

Cations-substrate interaction

The adsorption of Cu^{2+} and Ag^{+} cations on a glass substrate under the deposition conditions shown in the Table is discussed in details in this subsection. The Debye length k_1^{-1} given by the equation $k_1^{-1} = \left(4\pi I_B \sum_i z_i^2 n_i^0\right)^{-1/2}$ was equal to 1.12 and 4.35 nm in the case of Cu_xS and Ag_2S cationic solutions, respectively. I_B is, the Bjerrum length, given by the equation $q^2 / 4\pi\varepsilon_0\varepsilon_1 k_B T$, and it is equal to 0.7 nm at room temperature; z_i and n_i^0 are the valence and bulk number density of the i^{th} species of ions. Figures 7a and 8a represent the normalized free energy as function of the cationic solution pH and the distance in the case of [Cu^{2+}–glass substrate] and [Ag^{+}–glass substrate], respectively. The red lines in the same Figures correspond to the cationic solution experimental conditions. The surface charge densities were –0.076 and –0.204 C/m^2 in the case of [Cu^{2+}–glass substrate] and [Ag^{+}–glass substrate] interactions, respectively. The corresponding minimum distances, which correspond to the attached states, were 0.592 and 0.177 nm; and the normalized free energies were –1.849 and –45.98 in the case of [Cu^{2+}–glass substrate] and [Ag^{+}–glass substrate] interactions, respectively. In the absence of the surface charge, the normalized free energy was positive and the repulsion forces dominate. Figures 7b and 8b represent the normalized free energy as function of the surface charge and the distance d in the case of [Cu^{2+}–copper substrate] and [Ag^{+}–copper substrate], respectively. To make a comparison between the two substrates, we assumed that the copper substrate has the same surface charge densities as the glass substrate, i.e. –0.076 C/m^2 in the case of [Cu^{2+}–copper substrate] interaction and –0.204 C/m^2 in the case of [Ag^{+}–copper substrate] interaction. The minimum normalized free energies were deduced as –42.2 and –56.4 at the minimum distances of 0.0364 and 0.0417 nm in the case of [Cu^{2+}–copper substrate] and [Ag^{+}–copper substrate] interactions, respectively. At the same conditions, both the normalized free energies and the minimum distance were lower in the case of the copper substrate compared with that of the glass substrate. That is, the adsorption was better on the copper substrate than on the glass one, which explains the high adherence of the thin films deposited on copper substrate. The normalized free energies and the minimum distance at the non-charged copper substrate were –33.1 and 0.0364 nm in the case of [Cu^{2+}–copper substrate] and –8.3 and 0.0418 nm in the case of [Ag^{+}–copper substrate]. Therefore, contrary to the glass substrate case, the dominant interaction forces between cations and the copper substrate surface were attractive in the absence of the surface charge density.

Note that the cationic solution pH is a very important factor that affects the adsorption on metal oxide substrates. For example, the equilibrium separation between Cu^{2+} and the glass substrate decreased from 0.881 nm to 0.181 nm and the normalized free energy decreased from –0.125 to –39.748 when the cationic solution pH increased from 4 to 12. Finally, the cationic precursor solution concentration is also an important factor that affects the adsorption on metal oxide substrates. Ignoring the effect of the cationic solution concentration on the surface charge, the interaction between the cation Ag^+ and the glass substrate is depicted in Fig. 9, and, as we can see, the normalized free energy decreased with decreasing the cationic solution concentration, which means that better cations adsorption can be obtained at lower cationic solution concentrations.

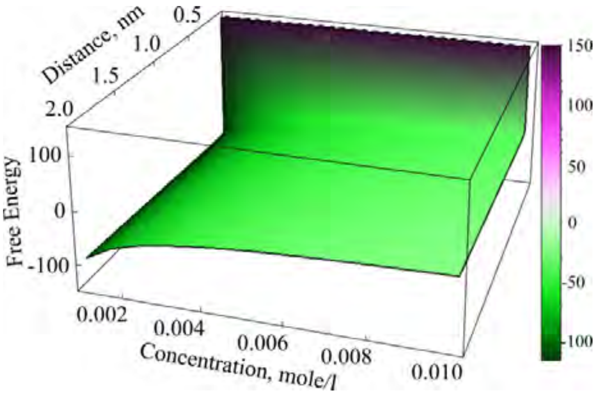


Fig. 9. Distance and cationic solution concentration of the normalized free energy of the cations Ag^+ near a glass substrate.

CONCLUSION

Adsorption phenomenon via the SILAR method was studied on two kinds of substrates: a dielectric (glass) substrate and a metallic (copper) one. A high pH of the cationic solution increases the glass surface charge density. Therefore, adding ammonia as complexant to the cationic solution will increase its pH and will enhance the cations adsorption. The metallic sulfide depositions by SILAR on copper substrates were better than on glass substrates. The adsorption of cations was higher at a low cationic solution strength. The reaction steps and nucleation of the reacted molecules on the substrate affect the adherence of thin films, a subject which is interesting as future research.

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Реферат

Проведена серия экспериментов по осаждению сульфида металла на стеклянных и медных подложках методом последовательного нанесения тонких пленок с помощью ионной адсорбции и реакции (метод SILAR). Этот метод, основанный на процессе адсорбции катионов, предполагает наличие сил Ван-дер-Ваальса и электростатических сил. Согласно теоретическому анализу, рассматриваемому в настоящей работе, равновесное расстояние между катионами и поверхностью подложки ниже в случае медной подложки, чем в случае стеклянной, что подтверждает результаты, полученные в экспериментах по методике SILAR. Поверхностный заряд стеклянной подложки сильно зависит от pH раствора. При отсутствии поверхностного заряда, доминирующие силы между катионами в растворе и стеклянной подложкой являются отталкивающими в отличие от случая с медной подложкой, когда силы притяжения доминируют даже, если поверхность имеет некоторый положительный заряд. Это исследование обогащает знания о параметрах оптимизации при изготовлении тонких пленок из халькогенидов металлов с хорошей адгезией.

Ключевые слова: тонкие пленки, метод последовательного нанесения слоев ионной адсорбцией и реакцией, адсорбция, халькогениды металлов, силы ван-дер-Ваальса, электростатические силы.