Russian Journal of General Chemistry, Vol. 73, No. 7, 2003, pp. 999–1004. Translated from Zhurnal Obshchei Khimii, Vol. 73, No. 7, 2003, pp. 1057–1062.

Ion Exchange of Silver(I) on Thin PbS Films as Influenced by Diffusion

N. N. Umarova, N. I. Movchan, R. A. Yusupov, E. A. Korolev, and V. P. Morozov

Kazan State Technological University, Kazan, Tatarstan, Russia
Kazan State University, Kazan, Tatarstan, Russia

Received June 28, 2001

Abstract — Ion exchange of silver(I) on thin polycrystalline PbS films in 10^{-5}–10^{-2} M aqueous solutions of $AgNO_3$ at 20–60°C was studied by X-ray fluorescence, atomic-absorption, and X-ray diffraction methods and by transmission electron microscopy. Since, under the given experimental conditions, diffusion of Ag(I) ions in a solid is the limiting stage of the process, the experimental kinetic dependences can be adequately described by the Fick equation for both "semi-infinite medium" and "restricted plane" at "steady source" of a diffusant on the surface.

Sulfide sorbents, being highly selective to *d* elements, are appropriate for removing toxic metals in chemical technology and concentrating them in analytical chemistry [1–4]. Ion exchangers based on thin films of metal sulfides and hydroxides are widely used to concentrate heavy metals from natural geothermal waters [5–8]. Published data on the sorption kinetics of a wide assortment of ions on dispersed sulfides (ZnS, CdS [9, 10], PbS [11], etc.) show that the sorption of metal ions proceeds by the ion-exchange mechanism. In [9, 10], the kinetic sorption curves were interpreted using the Erofeev equation of formal kinetics, where the main criterion is the rate constant of the heterogeneous process. The data on the sorption kinetics of Ag, Os, Ir, Pt, Au, Hg, Tl, Pb, Bi, Po, and U on thin-layer sulfide sorbents (ZnS, CdS, PbS, and CuS) were treated using the Langmuir model of the adsorption layer [5–8]. Various sorbate/sorbent pairs were compared using the distribution coefficients. The Langmuir model can be applied to heterogeneous processes only if the limiting stage of the ion exchange is the mass transfer of ions from solution to the film surface, which is realized in sorption of trace amounts of metal ions. The most important characteristic of inorganic ion exchangers is the coefficient of chemical interdiffusion of the exchanging ions through the growing phase of the reaction product, which is a milestone for mathematical description of more complex processes involving sorbents. However, there is yet no mathematical model satisfactorily explaining negative effect of some complexing agents (thiosulfate ion, thiourea, etc.) on the kinetics of heavy metal sorption by sulfides [4].

The diffusion coefficient is a very important parameter, because it allows comparison of various inorganic sorbents. However, the data on the coefficients of chemical diffusion for metal sulfides are scarce. For example, in [12] the volume diffusion coefficient of Ag(I) in the course of ion exchange on the surface of CdS single crystal was determined as $D = 2 \times 10^{-13}$ cm^2 s^{-1} (T 348 K); the estimated value of $D < 10^{-17}$ cm^2 s^{-1} for Ag(I) ions at room temperature in the bulk of $Cd_xHg_{1-x}Te$ crystal (x 0.55–0.80) was given in [13].

In this work we developed a methodological approach to evaluation of the diffusion coefficient of silver(I) ions from the data on the kinetics of Ag(I) ion exchange between aqueous solutions and thin polycrystalline films of lead sulfide PbS.

As seen from the X-ray diffraction (XRD) data, the PbS film prepared by chemical precipitation has the galena structure, which consists of two layers differing in the orientation of crystallites with respect to the support. The first layer growing directly on the inert support is a well-textured polycrystalline film. The texturing degree is so high that only the (100) planar networks (hereinafter, crystallographic planes) of PbS (Figs. 1a, 1b) are observed in the XRD patterns of the low-lying layers. Such orientation explains appearance of two galena reflections in (100) plane (d_{200} 2.98 and d_{400} 1.49 Å) and one reflection in (111) plane (d_{111} 3.44 Å). With increasing thickness of the PbS layer, the crystallite orientation becomes more random, and, finally, the diffraction pattern corresponding to the powdered sample is recorded (Fig. 1c). The ion exchange in aqueous $AgNO_3$ solutions changes

1070-3632/03/7307-0999 $25.00

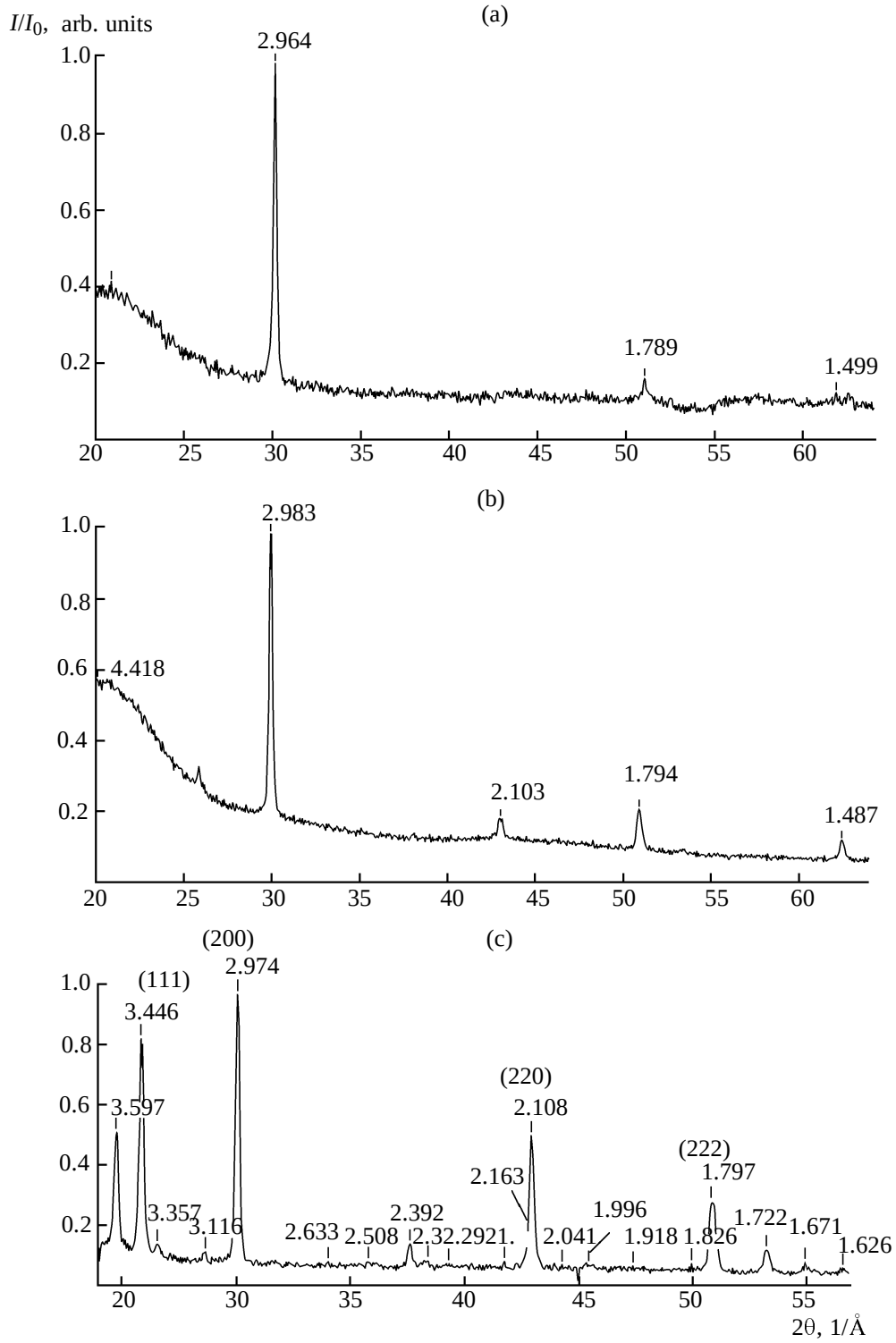

Fig. 1. Diffraction patterns of lead sulfide film of (a) minimal (<0.1 μm), (b) intermediate (0.1–0.3 μm), and (c) maximal (>0.3 μm) thickness.

the chemical composition of the thin-layer sorbent. It is known that at room temperature galena gradually converts into acanthite (modification of silver sulfide Ag_2S). In the diffraction patterns, this new compound is detected by the reflection d_{121} 2.64 Å.

With increasing time of the PbS film contact with $AgNO_3$ solution, the intensity of PbS reflections decreases, whereas the intensity of Ag_2S reflections (d_{121} 2.64 Å) increases (Fig. 2), which corresponds to the changes in the content of galena and acanthite

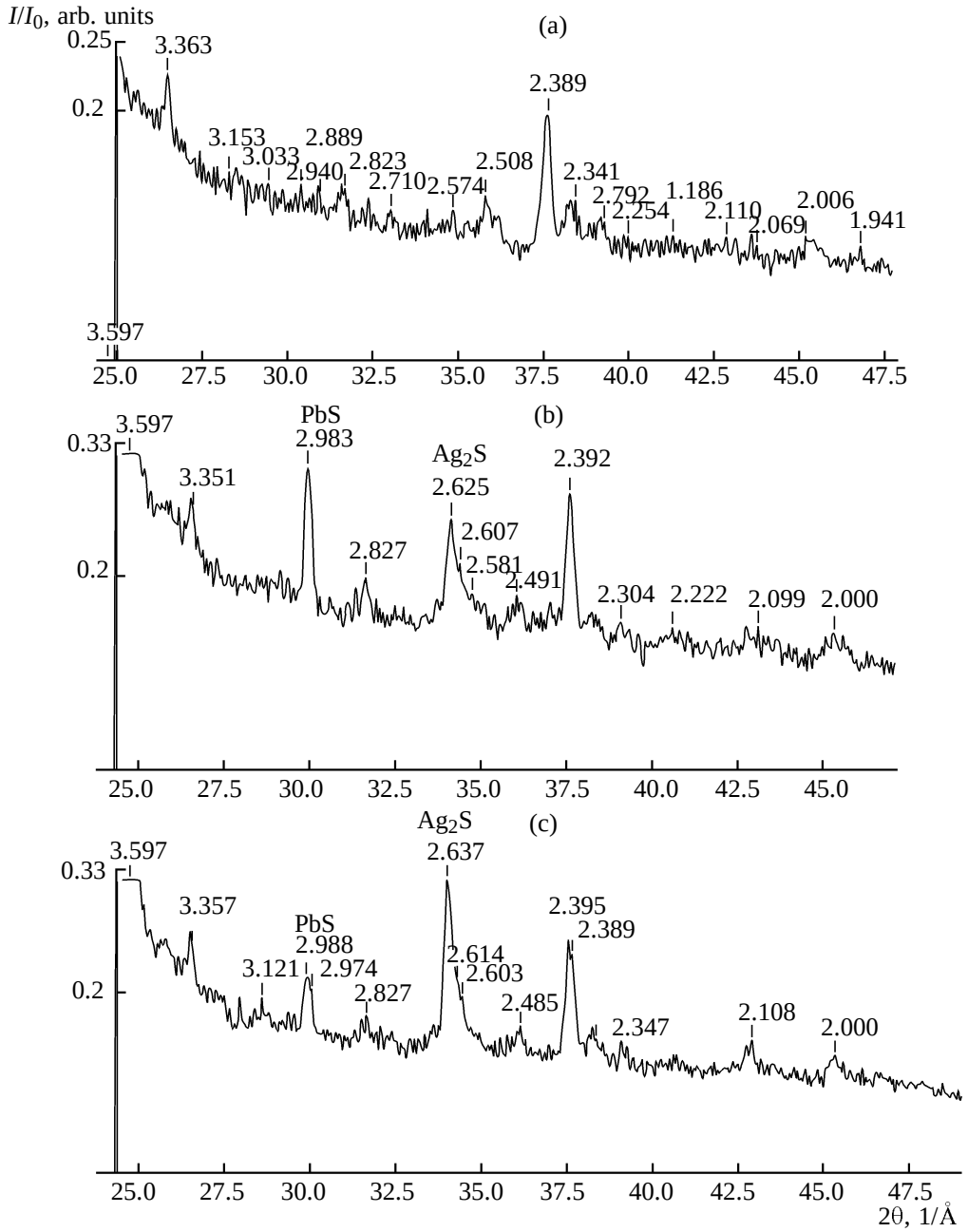

Fig. 2. Diffraction patterns of the surface of polyethylene terephthalate films (a) with no coating and (b, c) coated with a thin layer of PbS sorbent at various degrees of ion-exchange substitution by Ag_2S. Ion-exchange time at 50°C, min: (b) 25 and (c) 240.

phases in the metal sulfide film. The successive XRD measurements in the course of galena–acanthite transformation showed that acanthite is represented by a single reflection d_{121} 2.64 Å.

This feature is probably due to the growth of acanthite crystals on galena in certain crystallographic orientation, when crystallographic planes (121) of acanthite are located in parallel with galena crystallographic planes (111) and (100), which, in turn, are parallel to the support surface. These data suggest that the substitution of lead(II) sulfide with silver(I) sulfide proceeds with the structure inheritance. With increasing acanthite content, the size of the areas of the coherent scattering of its crystallites increases (up to 160 nm) in the direction perpendicular to the crystallographic planes (121). Such a trend suggests that the substitution of galena with acanthite in the PbS

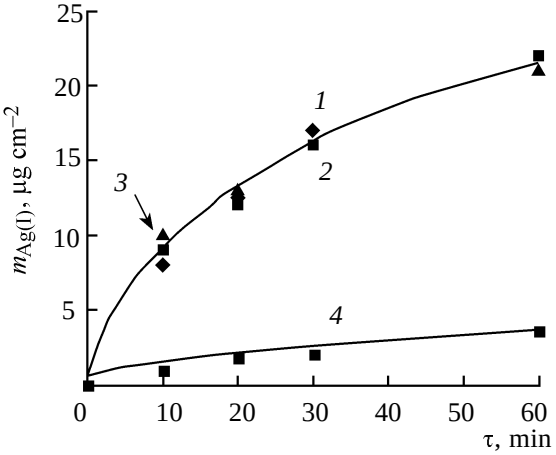

Fig. 3. Kinetic curves of Ag(I)/Pb(II) ion exchange on the PbS film surface at $AgNO_3$ concentration, M: (*1*) 10^{-2}, (*2*) 10^{-3}, (*3*) 10^{-4}, and (*4*) 10^{-5}.

film proceeds predominantly in the frontal area, i.e., acanthite crystallites move from the film surface into its bulk, substituting galena crystallites.

It should be noted that, due to the presence of grains (or crystallites) in thin polycrystalline films, chemical diffusion of ions in the solid phase should involve two processes: diffusion along the grain boundaries and diffusion inside the grains, whose rates can differ by several orders of magnitude [14]. The average size of PBS grains in the initial polycrystalline film (determined by measurements of the coherent scattering areas) are as follows: r_{200} 40 and r_{121} 25 nm. Similarly to the case of diffusion in the bulk samples, three types of the diffusion kinetics can be realized in thin films: A, B, and C [14]. The kinetics of type A means that the grain-boundary and bulk diffusion cannot be separated and, thus, the ion transfer is described by a single effective diffusion coefficient D_{ef} lying between the bulk D_b and grain-boundary (D_{gb}) diffusion coefficients. From the macroscopic viewpoint, such a system meets the Fick law requirements to a uniform system, where the diffusion front is planar and the isoconcentration profiles are parallel to the diffusant source, with the effective diffusion coefficient D_{ef}, and the penetration depth is proportional to $\tau^{1/2}$.

Under our experimental conditions, the kinetics of type C, when the diffusant penetration in the bulk is characterized only by the diffusion coefficient D_{gb}, is not realized, because the kinetic curves show that the degree of the ion-exchange completeness (F) is nearly 1, which is impossible in the case of the grain-boundary diffusion only. The kinetic of type B is proportional to $\tau^{1/4}$ and does not obey the Fick law. Hence, under our experimental conditions the kinetics of type A is most probably realized.

The kinetics of the Ag(I)/Pb(II) ion exchange was studied at various concentrations (from 10^{-2} to 10^{-5} M) of $AgNO_3$ in solution (Fig. 3). As seen, in the concentration range from 10^{-2} to 10^{-4} M the kinetic curves coincide. The activation energy of the ion exchange was evaluated from the kinetic measurements in the 298–343 K temperature range at $AgNO_3$ concentration of 3×10^{-3} M; its average value was determined as E_a 74 kJ mol^{-1}, which corresponds to the kinetic control of the process. At concentration smaller than 10^{-4} M, diffusion in the solid bulk probably loses its rate-limiting role, and sorption passes from the kinetic into the mixed mode, when the rate of the successive process is controlled by both diffusion in the solid and supply of the diffusant from solution to the film surface.

The diffusion coefficients can be calculated from the kinetic curves recorded under the conditions of kinetic control using two versions of the Fick equation for a "steady source" of a diffusant: for "semi-infinite medium" and "restricted plane." The first version was presented in [15] and its solution is given as Eq. (1) [16–18].

$$m(\tau) = 2c_0(D_\tau/\pi)^{1/2}, \quad (1)$$

where $m(\tau)$ is the weight of metal that diffused into the sorbent through its surface (g cm^{-2}) in time τ (s); c_0 is the surface concentration of the diffusant (g cm^{-3}); and D, here and hereinafter, is the effective diffusion coefficient (cm^2 s^{-1}). Since c_0 in the first approximation is equal to the density of the new Ag_2S phase, the ion-exchange equation can be presented as follows:

$$m(\tau) = 2\rho(D_\tau/\pi)^{1/2}, \quad (2)$$

where ρ is the acanthite density (g cm^{-3}). It should be noted that this equation is applicable at sorbent homogeneity and close densities of the exchanging phases. The electron-microscopic and XRD data confirmed the polycrystalline structure and homogeneity of the lead sulfide sorbent [19, 20]. The PbS film thickness determined by the electron microscopic analysis was ~0.4 μm, which well agrees with the value calculated from the density of individual PbS. The diffusion coefficient D evaluated with Eq. (2) was $(1.91 \pm 0.15) \times 10^{-15}$ cm^2 s^{-1} [15]. When the thin-film sorbent is used, the "semi-infinite medium" requirrement is disturbed and the "restricted plane" model is more adequate. Actually, the real kinetic curve recorded with a "steady source" of a diffusant is not a "pure" parabola; when plotting the curve in the $m(\tau)$–

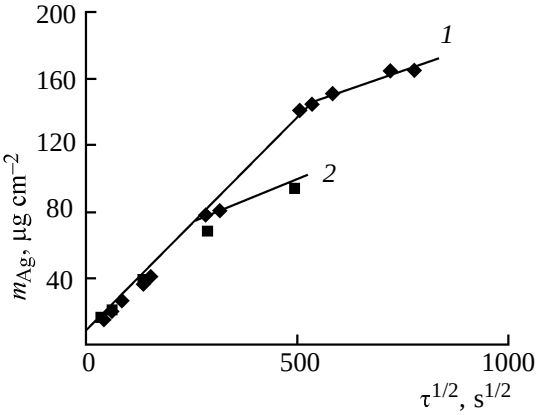

Fig. 4. Kinetic dependence for two PbS films of (*1*) 0.36 and (*2*) 0.10 μm thickness, plotted in the m_{Ag}–$\tau^{1/2}$ coordinates.

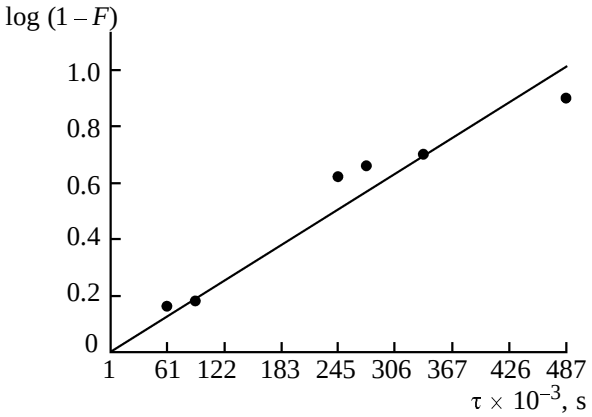

Fig. 5. Degree of the ion exchange completeness (*F*) as a function of time (semilog plot).

$\tau^{1/2}$ coordinates, we obtain the dependence whose linearity is lost at prolonged ion exchange (Fig. 4). In this case, the inflection points of the films of various densities correspond to various times of the ion exchange.

The Barrer method [21, 22] widely used in the study of ion-exchange kinetics is actually the solution of the Fick equation for a spherically symmetrical particle, where the main fixed parameter is the radius r of the ion-exchanger particle. Solution of the Fick equation for the "restricted plane" and "steady source" of a diffusant on the surface used in the case of the planar sorbent [boundary conditions: $C(x, 0) = 0$, $c(0, \tau) = c(l, \tau) = C_0$] can be approximately presented by Eq. (3) at $\tau > 0.35l^2/D$ with an accuracy of about 1% [18].

$$F = m(\tau)/m_0 = 1 - (8/\pi^2)\exp(-\pi^2 D\tau/l^2), \qquad (3)$$

where *F* in the degree of the reaction completeness; *l*, thickness of the "restricted plane" (film), and $m_0 = c_0 lS$, maximal amount of a diffusant that can enter into the sample with area *S*.

As seen from Fig. 5, the dependence (3) becomes a straight line in the log $(1 - F)$–τ coordinates, and *D* is determined from its slope. The diffusion coefficients obtained for two films with various thicknesses (0.1 and 0.36 μm) were equal and comprised 1.2×10^{-15} cm^2 s^{-1}. Thus, two different calculation procedures gave equal results. The only difference in the procedures is that the evaluation of *D* by the second procedure requires additional experimental measurement of the sorbent layer thickness. The diffusion coefficient obtained rafers to the real process, and the experimental $m(\tau)$–$\tau^{1/2}$ dependence describes the effect of the lead sulfide film thickness on the Ag(I)/Pb(II) ion exchange in solutions and allows prediction of the capacity of the thin-layer sorbents as influenced by the time of contact between the sorbent and solution.

EXPERIMENTAL

As the sorbent we used a thin polycrystalline film of PbS prepared by chemical deposition from solutions of thioamides [23] onto a planar inert (polyethylene terephthalate or cellulose triacetate) support 20 μm thick. The size of the support specially designed for X-ray fluorescence measurements was 28×28 mm. The thickness of the two-side polycrystalline PbS film obtained in different experiments varied from 0.1 to 0.5 μm, which corresponded to the PbS amount from 0.3×10^{-6} to 1.5×10^{-6} mol cm^{-2}. The required solutions were prepared using double-distilled water. Chemically pure or ultrapure grade $AgNO_3$ and $Pb(CH_3COO)_2$ were used without additional purification.

The quantitative analysis for the content of Ag and Pb in the solid phase was performed by X-ray fluorescence and atomic-absorption methods using a VRA-20L unit and AAS-IN device equipped with a flame atomizer, respectively. The standard solutions for atomic-absorption analysis were prepared from the weighed amounts of $AgNO_3$ and acidified to pH 1 (nitric acid). The lead content was analyzed using the reference solutions [GSO (State Reference Sample) 1842-80-1846-80] prepared at the ISARI Research and Production Association.

The XRD patterns were recorded on a GUR-3.0 (DRON-2.0) diffractometer, CuK_α radiation, λ

1.54178 Å, 6 s exposure time, and 0.05° scanning step. The film thickness was measured on a Hitachi-18 transmission electron microscope using the cross cuts of the film samples.

The ion exchange kinetics was studied by the restricted volume procedure under the steady-state conditions at 20–60°C in the $AgNO_3$ concentration range 10^{-2}–10^{-5} M, according to the procedure given in [15].

REFERENCES

1. *Metody razdeleniya i kontsentrirovaniya v analiticheskoi khimii* (Separation and Concentration Methods in Analytical Chemistry), Moskvin, L.N. and Tsaritsyna, L.G., Eds., Leningrad: Khimiya, 1991.
2. Disam, A., Tschöpel, P., and Tölg, G., *Fresenius Z. Anal. Chem.*, 1979, vol. 295, no. 2, p. 97.
3. Gregorowicz, Z., Stec, H., and Ciba, J., *Fresenius Z. Anal. Chem.*, 1980, vol. 303, no. 5, p. 381.
4. Music, S., *Isotopenpraxis*, 1985, vol. 21, no. 4, p. 143.
5. Betenekov, N.D., Gubanova, A.N., and Chuburkov, Yu.G., *Radiokhimiya*, 1981, vol. 23, no. 1, p. 21.
6. Suleimanova, N.A., Betenekov, N.D., and Kitaev, A.G., *Radiokhimiya*, 1981, vol. 23, no. 1, p. 30.
7. Betenekov, N.D., Kaftailov, V.V., Denisov, E.I., Egorova, Yu.A., Gubanova, A.N., and Puzako, V.D., *Radiokhimiya*, 1986, vol. 28, no. 5, p. 599.
8. Polyakov, E.V., *Radiokhimiya*, 1993, vol. 35, no. 1, p. 90.
9. Vol'khin, V.V. and L'vovich, B.I., *Kinet. Katal.*, 1970, vol. 11, no. 5, p. 1337.
10. Vol'khin, V.V. and L'vovich, B.I., *Zh. Fiz. Khim.*, 1975, vol. 49, no. 6, p. 1512.
11. Glistenko, N.I., *Tr. Voronezh. Gos. Univ.*, 1953, vol. 32, p. 79.
12. Bruzzoni, P. and Juttner, K., *Electrochim. Acta*, 1984, vol. 29, no. 12, p. 1665.
13. Lyubomirsky, I., Lyakhovitskaya, V., Triboulet, R., and Cahen, D., *J. Electron. Mater.*, 1997, vol. 26, no. 2, p. 97.
14. Kaur, I. and Gust, W., *Fundamentals of Grain and Interphase Boundary Diffusion*, Stuttgart, 1989.
15. Umarova, N.N., Movchan, N.I., Yusupov, R.A., and Sopin, V.F., *Zh. Fiz. Khim.*, 2000, vol. 74, no. 9, p. 1707.
16. Carslaw, H.S. and Jaeger, J.C., *Condition of Heat in Solids*, Oxford: Claredon, 1959, 2nd ed.
17. Pavlov, P.V. and Khokhlov, A.F., *Fizika tverdogo tela* (Solid-State Physics), Nizhni Novgorod: Nizhegorod. Gos. Univ., 1993.
18. Venetsianov, E.V. and Rubinshtein, R.N., *Dinamika sorbtsii iz zhidkikh sred* (Dynamics of Sorption from Liquid Media), Moscow: Nauka, 1983.
19. Osin, Yu.N., Umarova, N.N., Movchan, N.I., and Korolev, E.A., Abstracts of Papers, *XVIII Rossiiskaya konferentsiya po elektronnoi mikroskopii* (XVIII Russian Conf. on Electron Microscopy), Chernogolovka, 2000, p. 61.
20. Korolev, E.A., Morozov, V.P., Movchan, N.I., Umarova, N.N., and Barieva, E.R., *Izv. Vyssh. Uchebn. Zaved., Ser. Probl. Energet.*, 1999, nos. 11–12, p. 76.
21. Barrer, R.M. and Falconer, J.D., *Proc. Roy. Soc., Ser. A*, 1956, vol. 236, p. 227.
22. El-Naggar, I.M., Zakaria, E.S., Shady, S.A., and Aly, H.F., *Solid State Ionics*, 1999, vol. 122, nos. 1–4, p. 65.
23. Yusupov, R.A., *Candidate Sci. (Chem.) Dissertation*, Kazan, 1981.