PR-29. STUDY OF ETCHING PROCESS OF LEAD SULFIDE THIN FILMS

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Despite to wide application [1–3] lead sulfide thin films in opto- and microelectronic devices, the choice of the etching solution composition is difficult for them, because of no literary data about study of etching kinetics and mechanism. During the work, thermodynamic analysis and kinetics of PbS thin films etching by hydrochloric acid solutions, which also contained hydrogen peroxide and glycerol, were considered. Microstructure of thin lead sulfide films was studied as well.

Lead sulfide thin films were synthesized by hydrochemical deposition during to 90 min at 353 K. Reaction mixture contained lead acetate $Pb(CH_3COO)_2$, sodium citrate $Na_3C_6H_5O_7$, thiourea CSN_2H_4, ammonium iodide NH_4I and ammonium hydroxide NH_4OH. As substrates, we used sital plates, which were fixed in specially fluoroplastic devices and immersed into reaction mixture. Etching mixture was consisted HCl (11,6 M) and H2O2 (9,35 M) aqua solutions and glycerol (13,7 M).

To analyze ionic equilibrium with regard to the stability of the complex forms of lead in hydrochloric acid solutions, the solubility of its sulfide was calculated depending on the concentration of hydrochloric acid in the solution. It was shown that in the presence of ligand (Cl^-) and with decreasing pH, the equilibrium of the dissolution process of lead sulfide shifts to the right and the solubility increases.

To determinate the most probable mechanism of PbS oxidation with hydrogen peroxide, thermodynamic estimate of the change in Gibbs energy $\Delta_r G^0_{298}$ of possible reactions was carried out. It was shown that the most likely is the process of oxidation of Cl^- to ClO_4^- and S^{2-} to SO_4^{2-}.

During the kinetic studies, it was found that the dissolution rate of lead sulfide in the temperature range 298–323 K is from 3 to 40 nm · s^{-1}. According to the results of processing the kinetic curves of film etching, the particular kinetic orders for hydrochloric acid, hydrogen peroxide and glycerin were determined, which amounted to 2,6; 0,2 and 0,5, respectively. The activation energy of the Ea process, which was 48,1 ±1,0 kJ · mol^{-1}, was calculated, and the formal-kinetic equation for the lead sulfide etching rate was derived.

According to electron microscopic images of the obtained samples, it can be assumed that the process of etching of lead sulfide films is isotropic. During etching, the microcrystalline structure of the film is gradually destroyed and the surface is smoothed.

The results of kinetic studies and thermodynamic analysis allowed us to control the PbS etching process and optimize the composition of the etching solution for thin lead sulfide films in the photolithography process.

References

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