ABSTRACT

Tarnishing behaviours of lead, silver and their doped varieties in iodine atmosphere have been studied. The reaction temperature and partial pressure ranges chosen for lead-iodine system are 423-523 K and 0.615-6.578 kPa, respectively. The corresponding ranges for silver-iodine system are 333-373 K and 0.067-6.578 kPa. All the systems chosen in the present study are found to follow *parabolic law of film growth* processes. The iodide films have been characterised by SEM, EPMA, XRD and AES.Iodination studies have been carried out under normal and short-circuit conditions for both the systems.

Presence of Sb in Pb has enhanced the kinetics of iodide film growth process whereas that of Ag decreased it. Connecting a low impedance $Pt-$short-circuit path between the two interfaces [Pb/PbI_2 and $PbI_2/I_2(v)$] increases the rate further for Sb-doped Pb and pure Pb, and decreases for Ag-doped Pb. The iodine pressure dependence of rate constant of iodination has been found to follow $k_P \propto p_{I_2}^{1/2}$ under normal condition and that has been changed to $k_P \propto p_{I_2}^{1/3}$ under short-circuit condition for pure lead, Sb-doped Pb and Ag-doped Pb. The activation energy values for the film growth processes under normal condition in an iodine pressure of 0.615 kPa for Pb and Sb-doped Pb are found to be 64 kJ.mol^{-1}, and that for Ag-doped Pb is 84 kJ.mol^{-1}. However, these values have been reduced to 51 kJ.mol^{-1} and 66 kJ.mol^{-1}, respectively, under short-circuit condition. Results have been explained with the help of defect chemistry of PbI_2 lattice having a predominance of *Schottky defects*. The growth kinetics have been found to be the consequence of Wagner's electrochemical potential gradient induced migration of defect species for iodide growth on pure Pb and Sb-doped Pb where the film thicknesses are appreciably high. However, the driving force for migration of the defect species has been identified to be the Mott's electrical field gradient across the iodide layer on Ag-doped Pb system. Migration of positive holes and Pb-ions through the lead vacancies are the rate limiting steps under normal and short-circuit conditions, respectively. The values of hole and ionic conductivity as well as self-diffusivity of lead ions in PbI_2 lattices have been estimated from the kinetic data.

The effect of higher valent dopant like Cd in Ag has been found to decrease the rate of iodination under normal condition which suggests that the rate limiting step in

the film growth process is the migration of electron holes across the doped AgI layer as has been found for AgI growth on Ag. However, the iodination rate of Cd-doped Ag has been found to increase to a great extent compared to that of pure Ag under short-circuit condition which can be explained on the basis of ion migration mechanism. The pressure dependence of rate constant is found to follow a relation like $k_P \propto p_{I_2}^{1/2}$ for Ag and Cd-doped Ag under normal iodination condition. The corresponding relations are observed to be $k_P \propto p_{I_2}^{1/3}$ and $k_P \propto p_{I_2}^{1/4}$ under short circuit condition of iodination for Ag and Cd-doped Ag, respectively. Arrhenius plots have yielded identical activation energy values for film growth processes on both the systems which are found to be 25.8 kJ.mol^{-1} and 15.2 kJ.mol^{-1} under normal and short-circuit conditions, respectively. These values further suggest a change over in the mechanism of film growth process under shorting circuitry attachment. The experimental results have been explained with the help of defect equilibria considering the predominance of *Frenkel defects* in AgI and doped AgI lattices. The mechanism of film growth process has been confirmed to be Wagner's electrochemical potential gradient induced migration of defect species under normal as well as short-circuit conditions of iodination. The values of hole and ionic conductivity as well as self-diffusivity of silver ions in the resultant iodide lattices have been estimated through tarnishing studies.

KEY WORDS: Tarnishing; Iodination; Film growth kinetics; Undoped Pb; Ag-doped Pb; Sb-doped Pb; PbI_2; Schottky defects; Undoped Ag; Cd-doped Ag; $\beta - AgI$; Frenkel defects; Doping effect; Short-circuiting; Hole migration; Ionic migration; Conductivity; Diffusivity; Wagner's Parabolic Law; Mott's Parabolic Law.