

ELECTRICAL AND OPTICAL PROPERTIES OF AMORPHOUS $Pb_xIn_{25-x}Se_{75}$ FILMS WITH A DISPERSION OF NANOCRYSTALLITES

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Thin films of composition $Pb_xIn_{25-x}Se_{75}$ ($1 \leq x \leq 7$) have been prepared by thermal evaporation of the appropriate bulk materials on glass substrates. The grazing incidence X-ray diffraction patterns of the as-deposited $Pb_xIn_{25-x}Se_{75}$ films show two broad, low intensity peaks superposed on an amorphous background. The scanning electron microscope studies of the thin film samples revealed a nanocrystalline dispersion in an amorphous matrix. The SEM-EDAX analysis shows that the nanocrystalline regions have the same nominal composition as the entire film. Thin film deposition at lower substrate temperatures revealed a reduction in the size of the nanocrystalline particles. However, the nucleation of the crystallites could not be prevented even when the substrate temperature was reduced to 200K. Particle size was estimated from the width (FWHM) of the two peaks appearing in the x-ray diffraction pattern and SEM pictures. Thermo electric power measurements on the thin films revealed that the film with composition $Pb_{01}In_{24}Se_{75}$ was *p*-type and the films with composition $Pb_{03}In_{22}Se_{75}$, $Pb_{05}In_{20}Se_{75}$ and $Pb_{07}In_{18}Se_{75}$ were *n*-type semiconductors. d.c. electrical resistivity measurements on the thin films showed that the sheet resistance (ρ_{sheet}) decreased with an increase in Pb content. The optical band gap obtained from $(\alpha hv)^{1/2}$ versus hv plots for various $Pb_xIn_{25-x}Se_{75}$ films exhibited a decreasing trend with an increase in Pb content. The electrical and optical properties of these films have been interpreted in terms of existing models. To the best of our knowledge, this is the first report of majority charge carrier reversal in amorphous $Pb_xIn_{25-x}Se_{75}$ films with a dispersion of nanocrystallites.

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1. Introduction

Prior to the pioneering work by Tohge et al. which demonstrated that majority charge carrier reversal (MCCR) could be realized in bulk (*p*-type) amorphous germanium selenide with the addition of Bi [1,2] or Pb [3], the chalcogenide glasses were assumed to be strictly *p*-type semiconductors. This electronic transition is generally attributed to changes occurring in the Valence Alternation Pairs (VAPs) due the incorporation of metal additives [4-7]. Mehra *et al* [8] reported *p*- type to *n*-type carrier reversal in Pb doped In-Se glasses, which happens to be the only non-Germanium based chalcogenide glass to exhibit the MCCR phenomenon. Optical and electrical studies [8,9] on $Pb_xIn_{25-x}Se_{75}$ glasses showed that glasses with $x \geq 5$ at. wt. % Pb exhibited *n*-type conduction. The carrier reversal phenomenon in this glass system has been attributed to changes in the network matrix of In-Se glasses induced by the addition of Pb. The high electrical conductivity of the $Pb_xIn_{25-x}Se_{75}$ glasses and the lack of studies on thin films of this system motivated us to prepare amorphous Pb-In-Se films and to investigate their electrical and optical properties.

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2. Experimental

Thin film samples of composition $\text{Pb}_x\text{In}_{25-x}\text{Se}_{75}$ ($1 \leq x \leq 7$) were prepared from the powdered bulk starting material by thermal evaporation technique of the respective samples of the glasses under a vacuum of 10^{-5} Torr. In order to prepare the starting material for the deposition, weighed quantities of Pb, In and Se corresponding to desired composition were taken in fused silica ampoules. The ampoule was heated to 600 °C and homogenized at this temperature for 10 hours in the rotary furnace. Subsequently, the ampoule was cooled to room temperature. The alloy was powdered and used as the source for deposition. The amorphous nature of the as deposited samples was verified from the x-ray diffraction pattern obtained using a grazing incidence device (GID) attached to a powder X-ray diffractometer (Seifert 3003 TT). The compositional analysis for the above thin films was done using a Scanning electron microscope with energy dispersive X-ray analysis (SEM-EDAX, Jeol 5800) attachment. The X-ray diffraction (XRD) patterns of films deposited at about 310 K (during thermal evaporation the substrate holder temperature increases by 5° to 10 °C above the ambient) showed two crystalline peaks near 2θ values of 44.5° and 51°, respectively. In order to suppress the crystallization, the substrate was cooled with a liquid nitrogen container. The temperature of the substrate holder was measured with a calibrated PT100 sensor embedded on the substrate holder. Substrate temperature could be lowered to 200 K with such an arrangement. It was realized that mere reduction of temperature could not completely suppress the crystallization. However, the intensity of the two peaks reduced drastically signifying a reduction in nucleation of the crystalline phases. A corresponding broadening of the peaks with reduction in deposition temperature indicated a reduction in the size of the crystallites. XRD patterns of the thin films deposited at ambient temperature and 200 K are shown in Fig. 1. The average particle size was estimated by the analysis of the XRD data using the Scherrer's formula [10]. The particle size decreased when the films were deposited at lower (200 K) temperatures. The data reported in this paper correspond to the measurements performed on thin films deposited at 200 K.

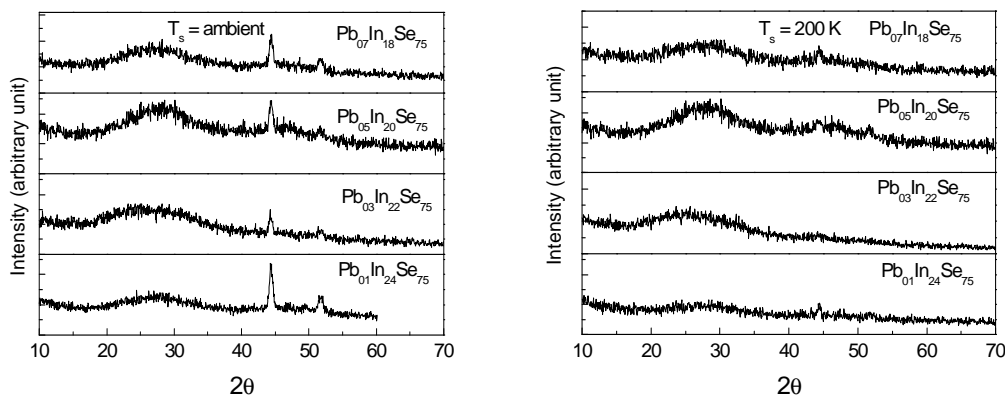


Fig. 1. XRD patterns of the Pb-In-Se thin films deposited at (a) ambient temperature and (b) 200 K.

Thermo electric power (TEP) measurement on the as deposited thin film samples was carried out using an indigenously fabricated set-up. The TEP set-up consisted of a low-pressure chamber with a poly tetra fluoro ethylene (teflon) sample holder equipped with PT100 temperature sensors and a resistance heater. With this arrangement, a temperature gradient could be maintained across the ends of the thin film sample and the thermo emf developed could be measured with an electrometer (Keithley 6512) under a low pressure of 10^{-4} Torr. As a convention, the hot end of the film was connected to the positive terminal and the cold end to the negative terminal of the electrometer. Since the Seebeck coefficient, $Q = -\Delta V/\Delta T$, a negative potential difference results in a positive Q which is the characteristic of a p -type semiconductor. On the other hand, a positive potential difference gives a negative Q , which is the characteristic of an n -type semiconductor. The set-up could provide Q values

with an error of $\pm 2\%$ in the temperature range of 300 K to 500 K. An analysis of the composition of all the films was done using a Scanning electron microscope (Jeol 5800) equipped with EDAX facility. The thickness of the thin films was measured using a commercial ellipsometer (Gaertner LXUV910). The film thickness was in range of 150 nm to 200 nm with an uncertainty of $\pm 2\%$. Optical absorbance of the films in the wavelength range of 300 nm to 900 nm was recorded with a dual-beam ultraviolet-visible-near infrared spectrophotometer (Shimadzu 3101 UVPC) with a blank substrate plate as reference. Optical band gap was calculated from the plots of $(\alpha h\nu)^{1/2}$ versus $h\nu$. d.c. electrical resistivity of the thin films was measured by the four probe method under a low pressure of 10^{-4} Torr in the temperature range of 300 K to 385 K. A constant current source (Keithley 220) and an electrometer (Keithley 6512) were employed in the measurements

3. Results and discussion

3.1. Structure

The XRD patterns of Pb-In-Se films shown in Fig. 1 show the presence of crystallites embedded in an amorphous matrix. XRD analysis (search and match with International Centre for Diffraction Data database) showed that the two crystalline peaks appeared at the same 2θ values in the case of all the samples and showed a good match with the powder diffraction file (PDF) data on crystalline Selenium (PDF no. 85-568) with hexagonal structure [lattice parameter $a = 3.956$, $b = 5.069$ with $\langle hkl \rangle = (0\ 1\ 2)$ and $(1\ 1\ -1)$ and corresponding 2θ values of 44.8° and 51.1° respectively and intensity values of 338 and 108, respectively]. Since no other combination of prospective elements (*viz.*, Pb, In, Se, O) gave any proximate match to these two peaks, it was presumed that crystalline Selenium in hexagonal structure is embedded in these amorphous films. The large width of the two peaks suggested that the size of these Se crystallites could be small. Figure 2 is a SEM photograph of $\text{Pb}_{01}\text{In}_{24}\text{Se}_{75}$, which shows that nanometer sized crystallites of Se (bright regions in Fig. 2) are embedded in the amorphous matrix. The relative area occupied by the crystallites is $\sim 10\%$ with respect to the overall film area. The SEM picture corresponds to the film deposited without cooling the substrate.

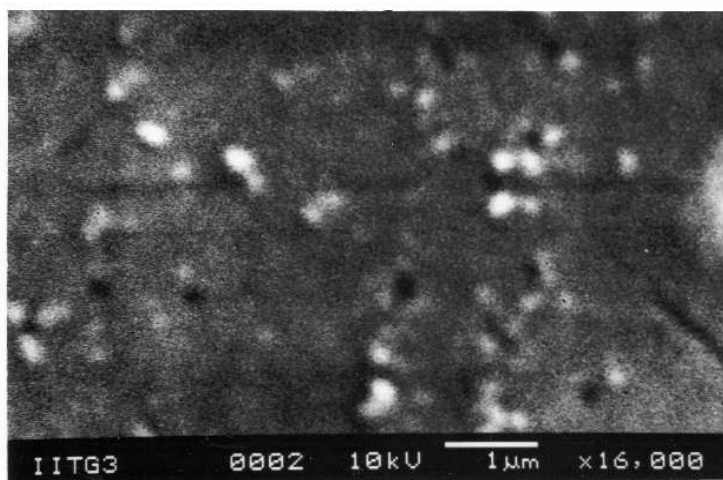


Fig. 2. SEM photograph of $\text{Pb}_{01}\text{In}_{24}\text{Se}_{75}$ glass (deposited without cooling the substrate) showing nanometer sized Se crystallites embedded in the amorphous Pb-In-Se matrix.

3.2 Electrical studies

Thermoelectric power measurements showed that the film with composition $\text{Pb}_{01}\text{In}_{24}\text{Se}_{75}$ was the only one to exhibit *p*-type conduction. The rest showed a negative Seebeck coefficient. The variation of Q measure at 348 K with Pb content is shown in Fig. 3a. From the slope of the least

squares fit to the Q versus $1000/T$ plots (Fig. 3b), the activation energy for the thermo electric power (E_s) of each film composition was calculated. The corresponding data are tabulated in Table 1.

Table 1. Seebeck coefficient, Activation energy for TEP and electrical conductivity, sheet resistance and band gap energy of Pb-In-Se glasses. The uncertainty in the data is given in parentheses.

| Sample composition | Q ($\text{mV}\cdot\text{K}^{-1}$) | E_s (eV) | E_σ (eV) | $\rho_{\text{sheet}} \times 10^8$ (ohm.m) | E_{opt} (eV) |
|--|---------------------------------------|-------------|-----------------|---|-----------------------|
| $\text{Pb}_{01}\text{In}_{24}\text{Se}_{75}$ | 3.43 (0.11) | 1.50 (0.07) | 1.13 (0.02) | 1.65 (0.05) | 1.76 (0.04) |
| $\text{Pb}_{03}\text{In}_{22}\text{Se}_{75}$ | -1.58 (0.05) | 1.21 (0.06) | 1.11 (0.02) | 1.34 (0.04) | 1.66 (0.03) |
| $\text{Pb}_{05}\text{In}_{20}\text{Se}_{75}$ | -4.82 (0.14) | 1.08 (0.05) | 0.63 (0.01) | 0.73 (0.02) | 1.61 (0.03) |
| $\text{Pb}_{07}\text{In}_{18}\text{Se}_{75}$ | -6.35 (0.19) | 0.99 (0.05) | 0.45 (0.01) | 0.70 (0.02) | 1.58 (0.03) |

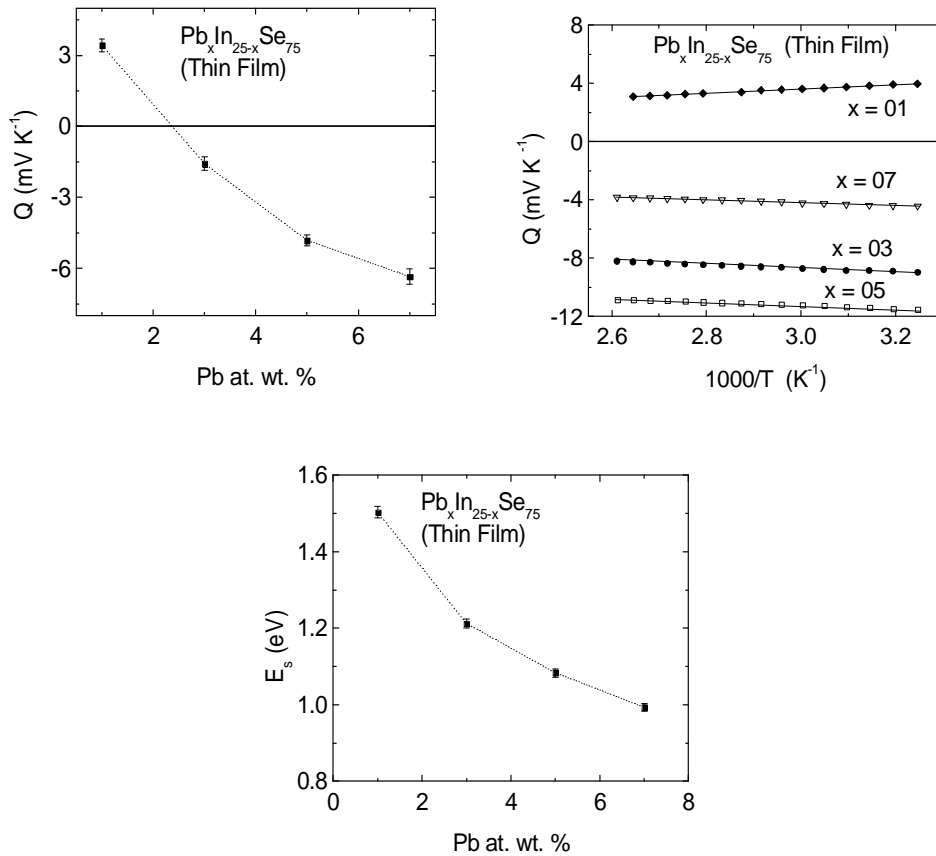


Fig. 3. (a) Variation of Seebeck coefficient with Pb content, (b) temperature dependence of Seebeck coefficient and (c) variation of activation energy of thermo electric power with composition of Pb-In-Se films.

The majority charge carrier sign reversal phenomenon observed in Pb-In-Se thin films can be interpreted in terms of Kolobov's proposal [11] of modifications in defect states with the addition of Pb. In the case of chalcogen atoms, the triply and singly coordinated defect states are Se_3^+ and Se_1^- , respectively. One can consider Se_3^+ as a hole-bearing atom. X-ray studies have confirmed [12] that Pb exists as Pb^{2+} in lead chalcogenide glasses. On addition of Pb to In-Se glasses, Pb^{2+} converts some

Se_3^+ into the Se_1^- state. As the number of Se_3^+ states decreases, the number of holes generated at the time of thermal excitation also decreases. Simultaneously, the number of Se_1^- increases. This results in the reduction of hole generating (triply coordinated and positively charged) defect states and at the same time increases the number of electron generating (singly coordinated and negatively charged) defect states. This disturbance in the concentration of the VAPs culminates in the unpinning of the Fermi level and shifts it towards the conduction band. These interpretations are consistent with the validity of the same in the case of Pb modified Ge-Se and Ge-Se-Te glasses [13].

The sheet resistance (ρ_{sheet}) of as deposited thin films of Pb-In-Se measured at 348 K is tabulated in Table 1. The composition dependence of ρ_{sheet} is depicted in Fig. 4a. The activation energy for electrical conduction (E_σ) calculated from the slope of $\ln(\sigma)$ versus $1000/T$ curves is listed in Table 1. The linearity of the $\ln(\sigma)$ versus $1000/T$ plots over the temperature range of 300 K to 385 K confirmed that the electronic conduction is due to a single conduction mechanism in this temperature range. The conduction mechanism is described as band transport and mathematically expressed as, $\sigma = \sigma_0 \exp(-E_\sigma/2kT)$ [14,15]. The variation of E_σ with composition is shown in Fig. 4b. The exponential decrease in the resistivity with increasing temperature results in lower ρ values at higher temperatures. A considerable drop in ρ_{sheet} is observed after 3 at. wt. % Pb, the composition at which the carrier reversal takes place. Similarly, a change of slope could be seen in E_σ versus Pb at. wt. % plot at the composition at which the carrier sign reversal is observed.

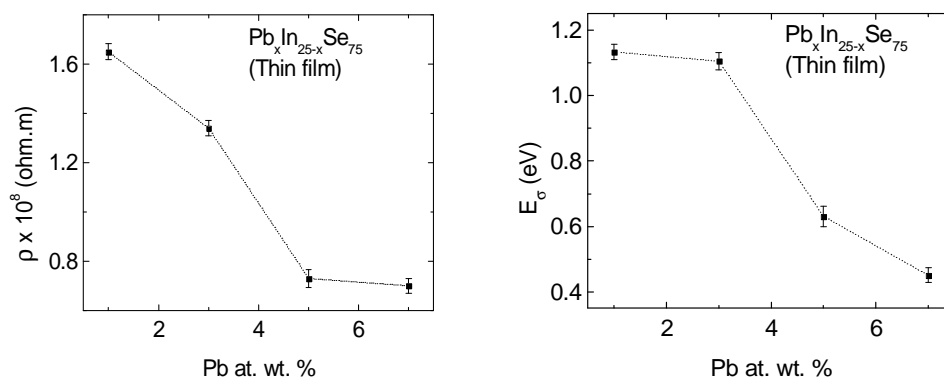


Fig. 4. (a) Variation of sheet resistance (at 348 K) and (b) activation energy for electrical conduction of Pb-In-Se thin films with composition.

3.3. Optical studies

Chalcogenide glasses are known to be direct band gap semiconductors [15]. A good linear fit obtained for the $(\alpha h\nu)^{1/2}$ versus $h\nu$ data at higher energies is the characteristic of direct band gap semiconductors (where α is the optical absorption coefficient, h the Planck's constant and ν is the photon frequency). $(\alpha h\nu)^{1/2}$ versus $h\nu$ plots obtained for Pb-In-Se thin films samples are shown in Fig. 5. The variation of optical band gap energy (E_{opt}) with composition is graphically shown in Fig. 6. The band gap energy of Pb-In-Se system decreases with an increase in Pb content. The optical band gap data is tabulated in Table 1. It can be observed from Fig. 6 and the data in Table 1 that the variation in E_{opt} is less for the n-type films.

The variation in E_{opt} of the thin films with change in Pb concentration could be understood on the basis of the change in the average bond energy of the amorphous film as a function of composition. Pauling proposed [16] that single covalent bond energy of heteronuclear bonds $D(\text{A-B})$ can be estimated from the single covalent bond energy of homonuclear bonds $D(\text{A-A})$ and $D(\text{B-B})$ and the electronegativity, x_{A} of atom A and x_{B} of atom B using the formula,

$$D(\text{A-B}) = [D(\text{A-A}) \times D(\text{B-B})]^{1/2} + 30(x_{\text{A}} - x_{\text{B}})^2 \quad (1)$$

The single bond energy values [17] of In-In (84.5 kJ.mol^{-1}), Pb-Pb (85.7 kJ.mol^{-1}) and Se-Se ($206.1 \text{ kJ.mol}^{-1}$) and Allred-Rockow electronegativity values were used for estimating the single covalent bond energies of In-Se ($257.5 \text{ kJ.mol}^{-1}$), Pb-Se ($231.2 \text{ kJ.mol}^{-1}$), etc. When Pb is added to $\text{In}_{25}\text{Se}_{75}$, Pb-Se bonds systematically replace In-Se bonds. Since the energy of the Pb-Se bond is lower than the In-Se bond, the average bond energy of the solid decreases as the Pb concentration is increased in $\text{Pb}_x\text{In}_{25-x}\text{Se}_{75}$. Since optical band gap is a bond sensitive property, a decrease in the average bond energy results in the decrease in the optical band gap energy of the film. Hence optical band gap decreases on addition of Pb to $\text{In}_{25}\text{Se}_{75}$ in the $\text{Pb}_x\text{In}_{25-x}\text{Se}_{75}$ films.

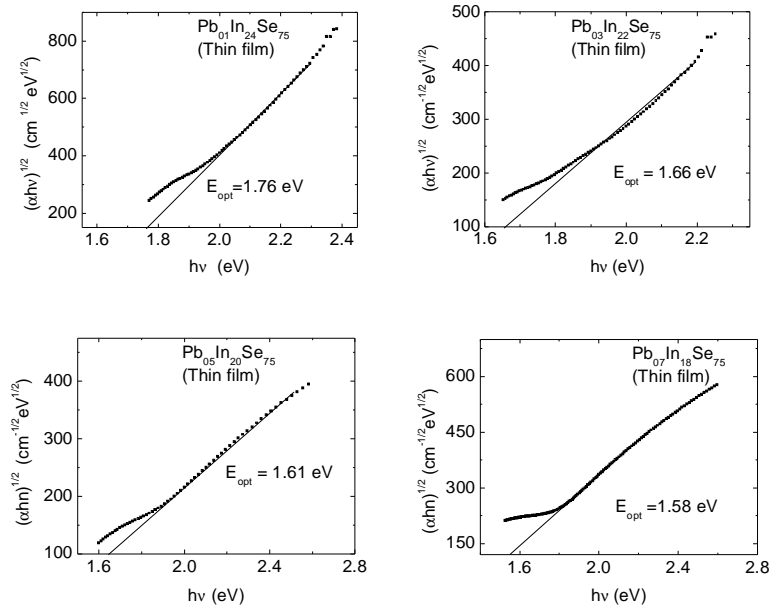


Fig. 5. $(\alpha hv)^{1/2}$ versus $h\nu$ plots of Pb-In-Se thin films.

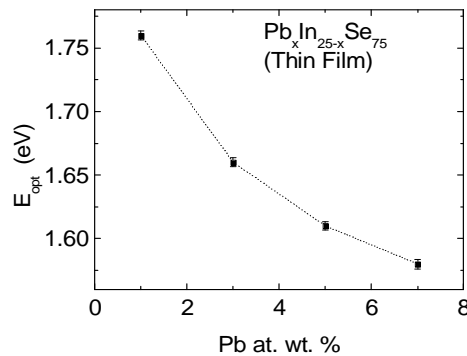


Fig. 6. Variation of optical band gap energy E_{opt} with composition of Pb-In-Se thin films.

4. Conclusion

Pb-In-Se thin films with a dispersion of Se nanocrystallites have been prepared by thermal evaporation of bulk material. The size of the nanocrystallites could be varied by controlling the deposition temperature of the films. The Pb-In-Se thin films exhibit a p - to n - type conduction type change as a function of composition. Seebeck coefficient (Q) at 348 K, activation energy for thermo electric power (E_s), sheet resistance (ρ_{sheet}) at 348 K, activation energy for electrical conduction (E_σ) and optical band gap of (E_{opt}) Pb-In-Se thin films deposited at 200 K were determined by

experimental measurement of the relevant physical entities. The d. c. conduction mechanism has been attributed to band transport mechanism. Composition dependence of Q and E_{opt} has been interpreted in terms of Kolobov's model and variation in average bond energy, respectively. The electrical and optical studies show that these properties are sensitive to the p- to n-type transition occurring in these films.

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