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The "Meyer-Neldel" Rule: Investigation and Application on Semiconductors

Thesis

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List of Symbols and Abbreviations

Symbol	Meaning	Symbol	Meaning
MNR	Meyer-Neldel rule	E_C	Conduction band energy
E_{MN}	Meyer-Neldel energy	DOS	Density of states
σ	Conductivity	a-	Amorphous
σ_o	Conductivity pre-exponential factor	$\hbar$	Planck's constant
σ_{oo}	Meyer-Neldel constant	$\langle r \rangle$	Coordination number
ΔE	Thermal Activation energy	Tg	Glass transition temperature
T	Temperature	SAW	Shimakawa and Abdel-Wahab
k	Boltzmann constant	YM	Yelon and Movaghar
nc	Nano crystalline	WC	Wang and Chen
XRD	X-ray diffraction	ΔS	Total entropy
EDXS	Energy dispersive X-rays spectroscopy	$\hbar\omega_o$	Optical phonons energy
FE-SEM	Field emission scanning electron microscopy	β	Integral breath
E_F	Fermi level	λ	Wavelength
MEE	Multi-excitation entropy	ε	Stress
EDD	Exponential energy distribution	D	Average grain size
E_g	Optical energy gap	α	Absorption coefficient

Abstract

Nanocrystalline lead selenide (*nc*-PbSe) thin films have been chemically deposited on glass substrates using appropriate chemical reagents in the aqueous alkaline media. The structural, morphological, optical and electrical characteristics of the prepared films have been studied. X-ray diffraction (XRD) analysis indicated that the films have a cubic structure with an average grain size of ~ 21 nm. The field emission scanning microscope (FE-SEM) micrograph shows that the films have a dense surface with a smooth granular structure and well defined grain boundaries. The temperature dependence of dc conductivity measurements $\sigma(T)$ were carried out under vacuum through a wide temperature range (77–350 K) for *nc*-PbSe films of thickness 375 ± 10 nm.

The application of Meyer-Neldel rule (MNR) is investigated under different circumstances for the as-prepared films. This includes thermal annealing with different time intervals through dc conductivity measurements, illumination with different light intensities and changing the ac frequency for electrical conductivity. The spread in the thermal activation energy of conduction (ΔE) is found to be correlated with the pre-exponential factor (σ_0) of the Arrhenius conductivity formula according to MNR.

The *nc*-PbSe prepared films have been irradiated with 2, 4 and 6 kGy of gamma at room temperature. The irradiation effects on the structural, optical and electronic properties of the films are discussed. Also, the application of MNR is studied through different conditions.

General Introduction

Early work in semiconductor quantum dots has focused on nanocrystals made of II-VI and III-V semiconductors. However, quantum dots of IV-VI semiconductors, such as the lead semiconductor compounds (PbS, PbSe, and PbTe) and the other IV-VI alloys cover the whole wavelength region between 3 and 30 μm ; provide a new and interesting area of research. The lead salts have a rock-salt crystal structure, narrow direct band gaps at the Γ points of the first Brillouin zone, and small effective masses for the charge carriers (*Mukherjee, Li, Gautam, Kar, & Shi, 2010*). Because of the small effective masses, both the holes and the electrons are strongly confined in nanometer crystals. A larger nanocrystal of a lead salt semiconductor can be used to obtain the same confinement energy as in a much smaller crystal of CdSe, as the Bohr exciton radius for PbSe (46 nm) is 8 times larger than that of CdSe (6 nm) (*Du et al., 2002*). The importance of this feature is that one can easily get a quantum confinement through this material. It is also noteworthy that PbSe has a very large optical index of refraction of ~ 4.6 and that lead to a promised material for photonic band gap applications. Tuning the optical band edge, while keeping a high optical constant, is an interesting possibility with PbSe quantum dots. Nevertheless, the ability to dope these nanocrystals with both holes and electrons has exciting possibilities for future optoelectronic applications (*Wehrenberg, Wang, & Guyot-Sionnest, 2002*).

On the other hand, little attention has been paid to the electrical properties and the presence of the MNR in the electrical conduction of PbSe thin films. In the case of a thermally activated dc electrical conduction (σ), the MNR states that the temperature-independent pre-factor (σ_0) of Arrhenius constant increases exponentially with increasing the activation energy ΔE as described in the following forms: