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Impact of Sulphate Bath Concentration on Structural and Magnetic Properties of Nifecr Thin Films

R.Kanagaraj[a*]
[a*]Department of Physics, Greentech College of Engineering for women,
Attur, Salem, Tamil Nadu, India
kanagarajphysics@gmail.com

R. Kannan[b]
[b]Department of Physics, KSR College of Engineering, Tiruchengode,
Tamil Nadu, India

S. Ganesan[c]
[c]Department of Physics, Government College of Technology,
Coimbatore, Tamil Nadu, India

S.K.Muthukumar[d]
[d]Department of Physics, Institute of Road and Transport Technology,
Erode, Tamil Nadu, India

Abstract: *Electroplated nano crystalline NiFeCr thin films have been successfully synthesized from sulphate bath at a constant current density (1 A/dm^2) by varying the sulphate bath concentration (0.1, 0.2, 0.3 and 0.4mol/lit). The structural, mechanical and magnetic properties such as coercivity, saturation magnetization were investigated for electrodeposited NiFeCr thin films. The SEM pictures of the electrodeposited NiFeCr thin films from the sulphate bath concentration of 0.1 mol/lit have no micro cracks and also the films have more uniform surface morphology as compared with the film coated from higher concentration. The sharp peaks in X-ray diffraction pattern of NiFeCr film reveals the crystalline nature and found to have BCC structure. From VSM results of the electroplated NiFeCr thin films, the various magnetic analyses such as coercivity, saturation magnetization were calculated. The hardness and adhesion of the electroplated films with substrate were also investigated. Reasons for variation in magnetic properties and structural characteristics of NiFeCr thin films coated from sulphate bath were discussed.*

Keywords: *Thin films, sulphate bath, sharp peaks, Coercivity and saturation magnetization.*

1. INTRODUCTION

NiFe based thin films have wider range of applications in MEMS (Micro Electro Mechanical System) and NEMS (Nano Electro Mechanical System). High magnetization, low coercivity, high permeability, nearly zero magnetostriction are the essential needs for the field of MEMS and magnetic recording heads. The well known soft magnetic alloy for MEMS is NiFe based thin films because of its soft magnetic properties [1-3]. Addition of alloying elements like Cr, W and Mo to NiFe alloys may improve the corrosion resistance and enhance the magnetic properties [4-9]. Cr is a good candidate as it is a highly corrosion resistant metal, chemically stable and also it have high melting point. The bath having Cr^{6+} ions are known to be toxic. At room temperature it is difficult to synthesis the thin films from the aqueous solution which contains Cr^{6+} ions. So that in this present work the solution containing trivalent chromium ions (Cr^{3+}) have been applied to an electrolyte for Cr electroplating [10]. Among the various physical and chemical deposition methods electrodeposition method is suitable process for NiFe based thin films because of its advantages like large scale production, easy to control the film thickness etc,. The crystalline size and growth orientation are the dominant factors to decide the magnetic properties of NiFe based thinfilms. These factors may be affected by current density, bath temperature and pH value etc. In this research work, the NiFeCr thin films are coated at the desired current density and bath temperature by varying the bath concentration.

2. EXPERIMENTAL PART

In the present work, the NiFeCr thin films are coated by varying the sulphate bath concentration from 0.1mol/lit to 0.4mol/lit. The bath composition and working parameters of electroplated NiFeCr thin

films are shown in the table 1. The NiFeCr thin films are electrodeposited from the sulphate bath at 30^0C with time period of 30 minutes. The pH value of the solution is maintained as 3. Both the anode and cathode (7.5 x 1.5 cm) are the aluminium substrates. The cathode substrate is covered with adhesive tape except the desired area of deposition. Before the electrodeposition, the substrates were polished with silicon carbide emery paper and degreased with 1M of NaOH for 5 minutes then rinsed with double distilled water and dried in air. The current density is 0.1 A/dm^2 for all the coated NifeCr thin films. The surface morphology and micro structure of the electrodeposited NiFeCr thin films were analysed with the Scanning Electron Microscopy (SEM) and X-ray diffraction (XRD). Vibrating Sample Magnetometer (VSM) is used to analyze the magnetic properties. The compositions of the thinfilms were studied by using Energy-dispersive X-ray Spectroscopy (EDAX) analysis. Vickers hardness tester (VHN) is used to determine the hardness of the deposited film.

Table1. *Bath composition and operating conditions of the electrodeposition bath*

Bath chemicals	Temperature (^{0}C)	pH	Bath concentration (mol / lit)
Nickel sulphate	30	3	0.1, 0.2, 0.3 and 0.4
Ferric sulphate			
Chromic sulphate			
Boric acid			
Glycine			
Ammonium formate			

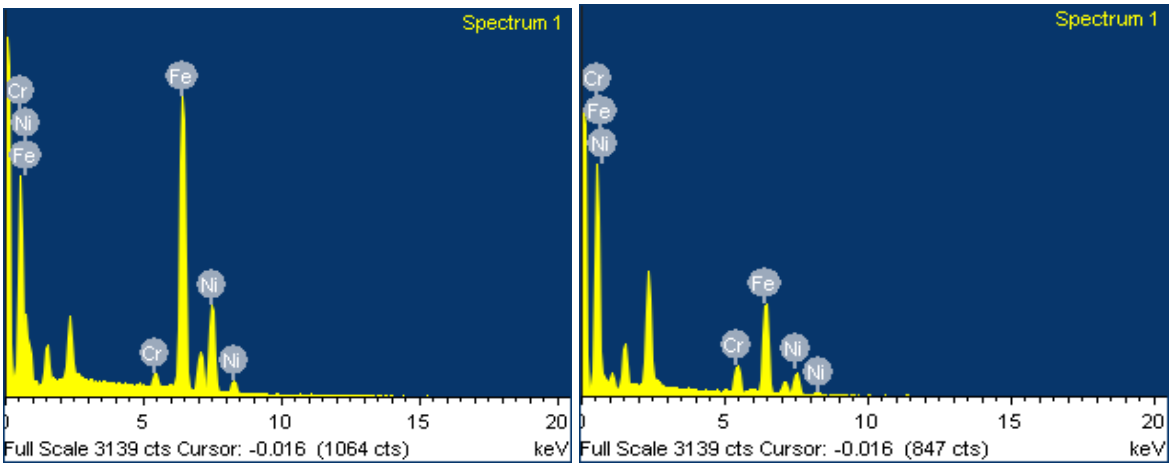
3. Results and Discussion

3.1. Elemental Composition of the NiFeCr Thin Films

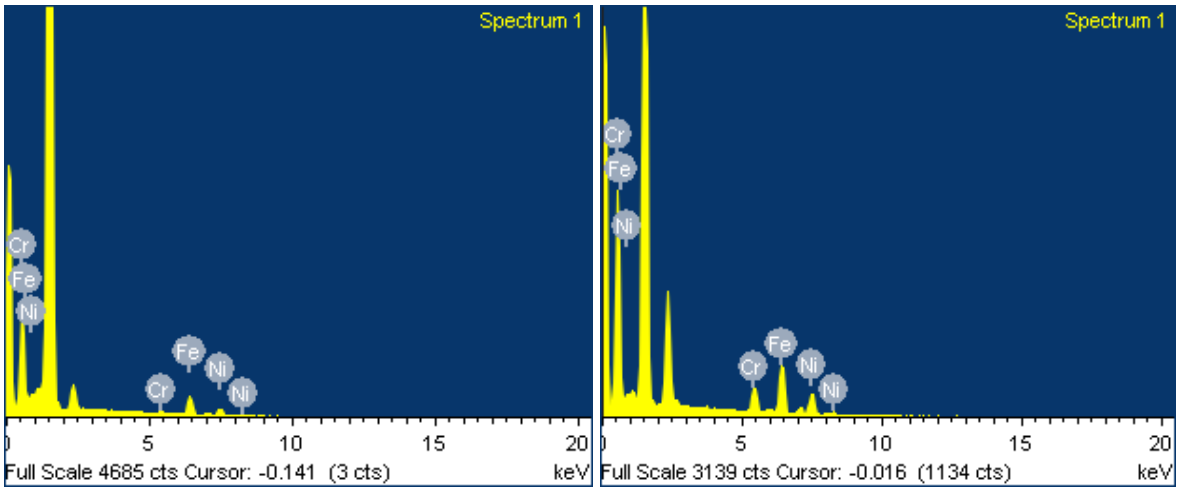
The elemental composition (Ni, Fe and Cr) of each electrodeposited NiFeCr thin film was confirmed by the EDAX analysis and it is shown in Fig. 1. The atomic weight percentage of Cr content present in the films were ranges from 6 to 16 wt% and Ni, Fe contents present in the NiFeCr films were shown in table 1. The atomic percent of Ni content present in the film decreases with an increment of bath concentration and it was almost equal to 25 % at the concentration of 0.4 mol/lit. All the coated films have lower Cr and Ni content. The Fe content increases with an increment of bath concentration. The NiFeCr thin films coated from sulphate bath at very low bath concentration have high Ni content with lower Cr content which may be used for magnetic applications.

Table1. *EDAX analysis of NiFeCr thin films*

S.No	Bath concentration (mol/lit)	Ni wt %	Fe wt %	Cr wt%
1	0.1	35.04	58.84	6.12
2	0.2	32.24	51.14	16.62
3	0.3	31.56	66.47	1.98
4	0.4	24.49	63.44	12.07



(a) **(b)**

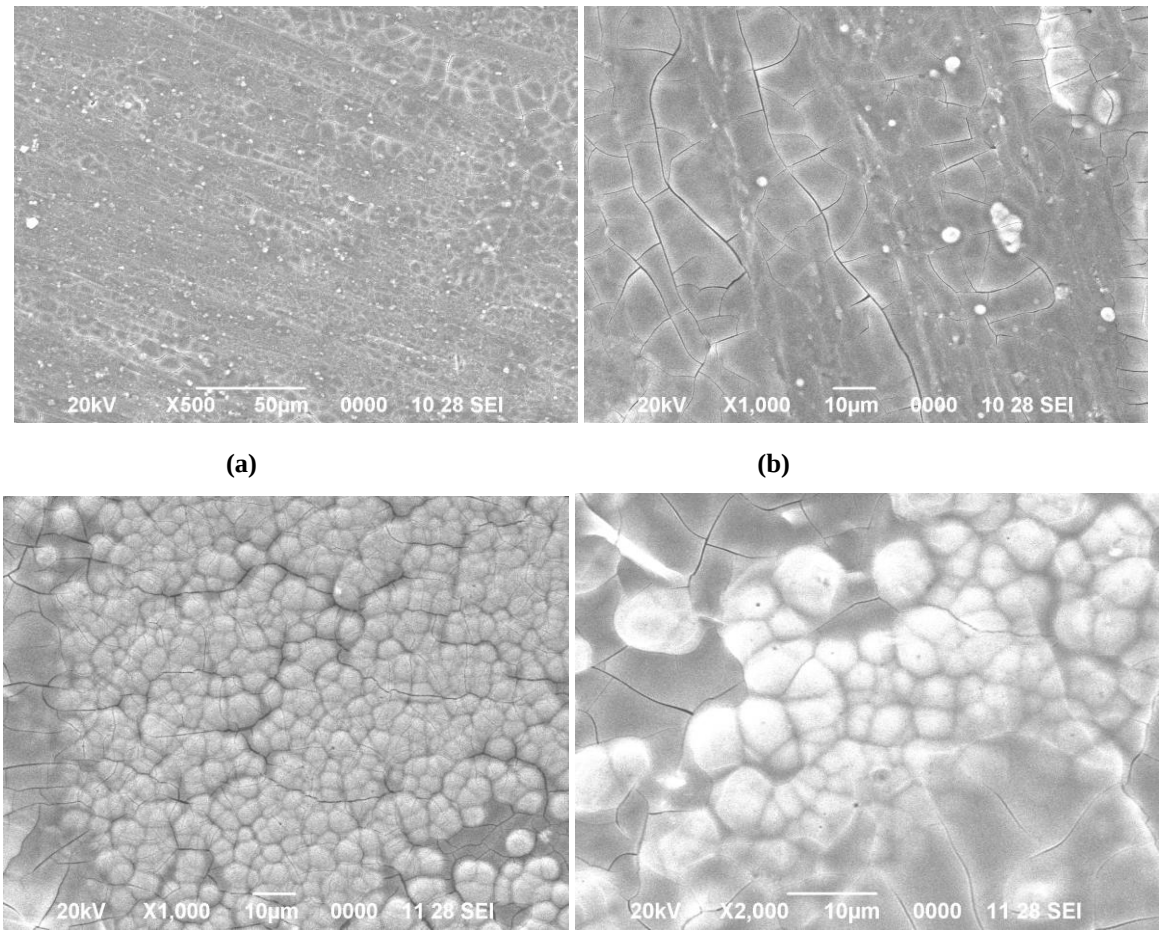


(c) **(d)**

Fig1. *EDAX spectrums of NiFeCr films coated from sulphate bath concentrations of (a)0.1 mol /lit (b) 0.2mol /lit (c) 0.3 mol /lit (d) 0.4 mol /lit*

3.2. Surface Morphology of the NiFeCr Thin Films

Scanning electron micrographs of electrodeposited NiFeCr thin films from sulphate bath are shown in Fig. 2. The NiFeCr films are obtained from different sulphate bath concentration have no micro cracks at lower bath concentration. At a low bath concentration, the surface is uniform, bright and smooth. At a bath concentration of 0.3 and 0.4 mol / lit, the surface is bright which indicates the ball like structure. The films coated at high sulphate bath concentration have some micro cracks. This is mainly due to the increment of Fe content and internal stress.



(a) **(b)**

(c) **(d)**

Fig2. *SEM images of NiFeCr films coated from sulphate bath concentrations of (a) 0.1 mol /lit (b) 0.2mol /lit (c) 0.3 mol /lit (d) 0.4 mol /lit*

3.3. X - Ray Diffraction Analysis of the NiFeCr Deposits

The X-ray diffraction pattern of electrodeposited NiFeCr films from sulphate bath at different concentrations of 0.1, 0.2, 0.3 and 0.4mol/lit as shown in Fig. 3.

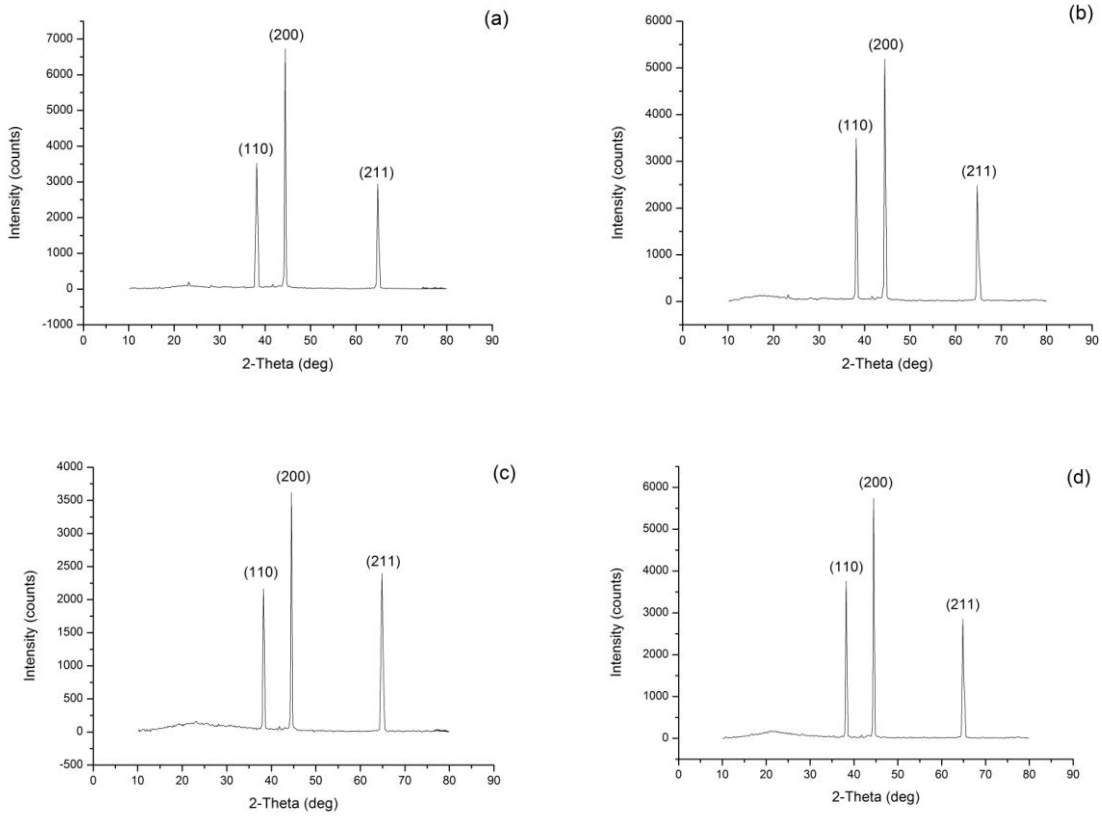


Fig3. *XRD patterns of NiFeCr films coated from sulphate bath concentrations of (a) 0.1 mol /lit (b) 0.2mol /lit (c) 0.3 mol /lit (d) 0.4 mol /lit*

The presence of sharp peaks in electroplated NiFeCr thin films indicates that the films were crystalline in nature. Crystalline sizes of the NiFeCr films were calculated from the XRD pattern using the Sherrors formula. Calculated values from XRD pattern clearly show that the crystalline sizes of the NiFeCr thin films are in the nano scale. The impact of bath concentration on the structural properties of NiFeCr thin film deposited from sulphate bath is shown in Table 2. The XRD patterns of NiFeCr films revealed the existence of BCC phase with (110), (200) and (211) diffraction peaks. The lowest crystalline size of 40 nm has been observed for NiFeCr thin film which is coated from bath concentration of 0.3mol/lit. The dislocation density of all the coated films has low value which indicates the purity of the film.

Table2. *Effects of bath concentration on structural properties of NiFeCr thin films*

Bath concentration (mol/lit)	**2θ (deg)**	**θ (deg)**	**Particle size, D (nm)**	**Strain (10^{-4})**	**Dislocation density ($10^{14}/m^2$)**	**D (A^0)**	**Full width half maximum β (10^{-3}) (radian)**
0.1	44.409	22.20	42.727	8.519	5.477	2.038	3.680
0.2	44.422	22.21	42.654	8.532	5.496	2.037	3.681
0.3	44.502	22.25	40.265	9.041	6.168	2.034	3.907
0.4	44.476	22.23	42.328	8.597	5.581	2.035	3.716

3.4. Mechanical Properties of the Deposits

Adhesion of the film with the substrate is tested by bend (bending the film with substrate to 180°) test and scratch test. This test shows that the NiFeCr thin films coated from sulphate bath have good adhesion with substrate. Hardness of the NiFeCr thin films were found to be about 91 VHN, 93VHN, 96 VHN and 97.5 VHN for the sulphate bath concentrations of 0.1, 0.2, 0.3 and 0.4mol/lit respectively.

Table3. *Micro hardness values of NiFeCr thin films*

S.No	Bath concentration (mol/lit)	Vickers hardness(VHN)
1	0.1	91
2	0.2	93
3	0.3	96
4	0.4	97.5

3.5. Magnetic Properties of the NiFeCr Deposits

Fig. 4 shows the BH loop of NiFeCr alloy thin film deposited at different sulphate bath concentrations of 0.1, 0.2, 0.3 and 0.4mol/lit. The magnetic properties of NiFeCr films were observed from vibrating sample magnetometer and are tabulated as shown in Table 4. The important parameters like grain size, bath temperature, bath concentration, pH value etc., have great impact on magnetic properties of electrodeposited NiFeCr alloy thin films. Grain size plays a major role to decide the magnetic properties of NiFe based thin films.

Generally single magnetic domains are easier to rotate when it is subjected to magnetic field instead of a larger domain. From XRD it was observed that, all the coated films have smaller crystalline size. Therefore, smaller grain size implies in smaller magnetic domains which are easy to rotate and in addition it decrease the coercivity.

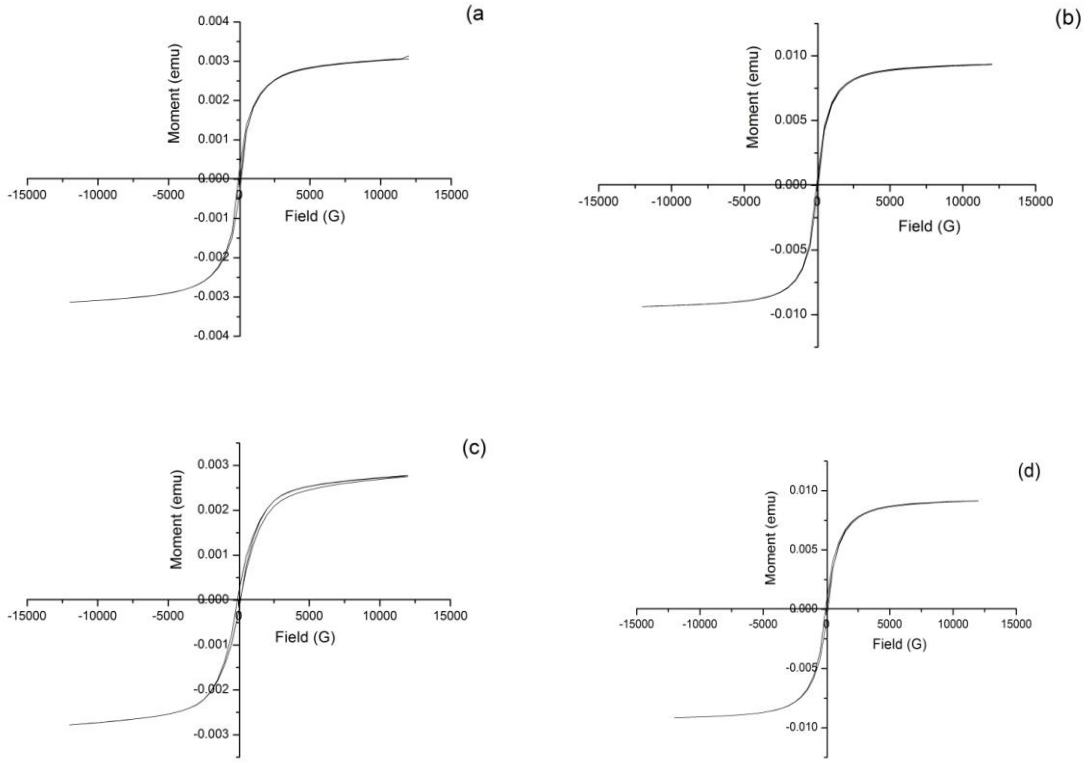


Fig3. *VSM results of NiFeCr films coated from sulphate bath concentrations of (a) 0.1 mol /lit (b) 0.2mol /lit (c) 0.3 mol /lit (d) 0.4 mol /lit*

Table4. *VSM results of NiFeCr thin films*

Bath Concentration (mol/lit)	Coercivity(G)	Magnetisation M_s 10^{-3} emu	Retentivity M_r 10^{-6} emu	Squareness S 10^{-3} (M_r/ M_s)
0.1	98.533	3.133	316.68	101.078
0.2	51.918	9.358	516.25	55.166
0.3	110.90	2.778	216.40	77.897
0.4	93.055	9.146	810.04	88.572

Maximum value of magnetization 9.358 emu/g with lower coercivity of 51 Gauss for NiFeCr thin films were obtained at the bath concentration of 0.2mol/lit. The films coated from high sulphate bath

concentration have higher have higher value of coercivity which reduces the saturation magnetization. This may due to the presence of higher Fe content in NiFeCr thin films. For sulphate bath, we concluded that the NiFeCr thin films coated at lower concentration exhibit the best soft magnetic nature compared with the NiFeCr thin films coated at higher bath concentration.

4. CONCLUSIONS

In this research work, NiFeCr films were electroplated from the sulphate bath at 30°C. The effects of sulphate bath concentrations on the structural, compositional, morphological and magnetic properties of NiFeCr thin films were analyzed. The electrodeposited NiFeCr thin film has body centered cubic structure. The crystalline size of the NiFeCr films was found to be in few tens of nano meters. The Ni content present in the NiFeCr film decreases with an increment of sulphate bath concentration. The presence of Cr content are in low range for all the coated deposits. The deposits were uniform and granular coated from 0.1 mol / lit. The high value of magnetization has been obtained for NiFeCr thin films coated from 0.2 mol / lit. The NiFeCr thin films have maximum value of hardness as 97.5 VHN was obtained at 0.4 mol / lit. It was concluded that, the NiFeCr thin films coated from the sulphate bath concentration of 0.2 mol / lit exhibits the best soft magnetic nature which may be used well for the MEMS (Micro Electro Mechanical Systems) applications.

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AUTHORS' BIOGRAPHY

R.Kanagaraj, received the M.Sc degree in physics from St.Joseph's College, Tiruchirapalli, India, in 2009. He is currently working towards the Ph.D. degree in physics at the Anna University, Chennai, India. His area of research is synthesis and magnetic characterization of NiFeCr thin films. So far he published five papers in peer reviewed international journals.

Dr. R. Kannan, Assistant Professor, Department of Physics, K.S.R. College of Engineering, Tiruchengode, India. He received the Ph.D. degree from Anna University, Chennai, India, in 2014. He is working in the area of synthesis and characterization of soft magnetic thin films and characterization of nano materials. So far he published twenty five papers in peer reviewed international journals.

Dr. S. Ganesan, Professor and Head of Physics in Government College of Technology, Coimbatore, India. So far he Published 85 papers in internationally reported Journals. He is authored four text books in the field of Engineering Physics. His research focuses on nonlinear dynamics, Thin films, Material science, Nanotechnology and Applied Physics. Thirteen scholars have completed their Ph.D. under his supervision and four scholars doing their Ph.D.

S.K.Muthukumar, Associate Professor, Department of Physics, Institute of Road and Transport Technology, Erode – 638 316, India. He received the B.Sc., and M.sc., degree from Bharathiyar University (NGM College, Pollachi) and M.Phil degree from the same university. His area of research includes material science, electronics and Thin films. He has 30 years of academic experience in a reputed College.