

**GROWTH AND INVESTIGATIONS OF CO-BASED  
SPIN GAPLESS SEMICONDUCTING EQUIATOMIC  
QUATERNARY HEUSLER ALLOY THIN FILMS FOR  
SPINTRONIC APPLICATIONS**

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**Growth and Investigations of Co-Based Spin Gapless  
Semiconducting Equiatomic Quaternary Heusler Alloy  
Thin Films for Spintronic Applications**

By

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Submitted

in the fulfilment of the requirement of the degree of the Doctor of Philosophy

to the



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*Dedicated to my Father*

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## **Certificate**

This is to certify that the thesis entitled “**Growth and Investigations of Co-Based Spin Gapless Semiconducting Equiatomic Quaternary Heusler Alloy Thin Films for Spintronic Applications**”, which is being submitted by **Mr. Vireshwar Mishra** to the **Indian Institute of Technology Delhi**, New Delhi, for the award of the degree of **Doctor of Philosophy** in Physics, is a record of bonafide research work carried out by him. He has worked under my supervision and guidance and has fulfilled the requirements for the submission of this thesis, which, in my opinion, has reached the requisite standard.

The results contained in this thesis have not been submitted, in part or full, to any other University or Institute for the award of any degree/diploma.

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# Abstract

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The spin gapless semiconductors (SGSs) are an intriguing class of novel quantum materials that bridge the gap between semiconductors and ferromagnets due to their peculiar band structure with zero band gap for one spin channel and semiconducting band gap for another spin channel. The presence of SGS characteristics in Heusler alloys, especially in Co-based Heusler alloys is even more promising because of their high Curie temperature ( $T_C$ ) and tuneable electronic and magnetic structure; hence they can act as a suitable replacement for diluted magnetic semiconductors (DMSs). Nowadays, Co-based equiatomic quaternary Heusler alloys (EQHAs) with 1:1:1:1 stoichiometry are in huge focus as they possess higher spin diffusion length compared to that of pseudo ternary alloys. Some of these compounds have reportedly shown SGS like characteristics.

In this thesis work, we have grown and studied two Co-based EQHAs thin films: CoFeMnSi (CFMS) and CoFeCrGa (CFCG). The study involves structural, magnetic and transport properties. Other than these two alloys, an insulating oxide  $MgAl_2O_4$  (MAO) was also grown for perpendicular magnetic anisotropy (PMA) related study in MAO/CFMS/MAO heterostructures and were characterized for structural, magnetic, morphological, and spectroscopy-based studies. The W and Ti materials were used as a protective capping layer in these heterostructures.

First, the highly ordered phase of CFMS thin film (~60nm) was optimized over Si (100) substrate and different structural, compositional, magnetic and transport measurements were performed so as to assess the SGS characteristic of the film. The ordered phase of CFMS film with negative temperature coefficient of resistivity and nearly temperature independent carrier concentration and mobility found to obey the SGS criteria.

After the phase optimization and successful verification of SGS behaviour, very next we have grown ~50nm thin CFMS sample and studied for *anomalous Hall effect* (AHE) and *weak localization* (WL) phenomenon. The fitting of the longitudinal conductivity data through *two-carrier model* suggested the presence of disorder film sample. The scaling of anomalous Hall resistivity/conductivity through different models justified that the AHE in CFMS is majorly governed by an intrinsic scattering mechanism due to the momentum space Berry curvature. The experimental value of *intrinsic anomalous Hall conductivity* ( $\sigma_{AH}^{int}$ ) was achieved to be around 37.75 S/cm, which is found to be considerably larger than the theoretically predicted value for

perfectly ordered CFMS structure and is possibly caused by elemental disorder present in CFMS film sample. The WL behaviour was justified by the presence of sharp negative cusps in magnetoresistance (MR) curves in low magnetic field regime up to 1T. Further justification of which is done via intercomparison between phase coherence length, mean free path, prefactor and sample size. The phase coherence length and prefactor are extracted by fitting the conductivity correction curves through Hikami-Larkin-Nagoaka (HLN) model, mean free path is derived from the carrier concentration which itself is evaluated from AHE data and sample size is taken as the thickness of the film.

In the very next study PMA is realized in MAO/CFMS/ MAO/Ti heterostructures annealed at 300°C and 400°C. We show that interfacial PMA is very responsive to the annealing temperature and the CFMS layer thickness ( $t_{CFMS}$ ). A large PMA is achieved for  $t_{CFMS} = 2.0$  nm. An improvement in the out-of-plane saturation magnetization with PMA is found to get remarkably stimulated by the bottom MAO/CFMS interface. Besides, a uniaxial PMA is observed for an as-deposited stack with  $t_{CFMS} \leq 1.5$  nm. Annealing at 400°C significantly promoted adequate interfacial oxidation with the improved thermal stability of the heterostructure. Through X-ray photoelectron spectroscopy, the formation of Co–O bonds occurring as a result of the hybridization of Co-3d<sub>z<sup>2</sup></sub> and O-2p<sub>z</sub> orbitals at the interface shared by CFMS with MAO is identified as the microscopic origin of the observed PMA in these stacks. These findings indicate that the CFMS and MAO-based structures have immense potential for the next generation spintronic devices.

The study of PMA is further extended by investigating PMA in MAO/CFMS/MAO/W stacks. A maximum effective PMA energy density ( $K_{eff}$ ) of  $\approx 2.48 \times 10^6$  erg/cc is observed when the thickness of the MAO layers ( $t_{MAO}$ ) is 1.5 nm. The development of the PMA and saturation magnetization ( $M_s$ ) is significantly stimulated by the structural changes at the MAO/CFMS and CFMS/MAO interfaces owing to the adequate interfacial oxidation state while tuning CFMS and MAO thickness. The study demonstrates that controlling the oxygen diffusion across the adjoining interface could be an easier means of achieving specific magnetic properties. These results open a new path towards the realization of novel spintronic devices employing PMA.

Finally, we have performed various structural, magnetic and transport measurements over an optimized CoFeCrGa Heusler alloy thin film (~50nm) grown over Si (100) substrate using industry-viable magnetron sputtering technique. The grown film showed *A2*-ordering under the

given set of X-Ray diffraction measurements conditions with saturation magnetization of  $1.86 \mu_B/\text{f.u.}$  (at 5K) and Curie temperature  $\sim 595\text{K}$ . Nearly linearly varying longitudinal resistivity with negative temperature coefficient was observed. Fitted longitudinal conductivity curve through “*two-carrier model*” gives slight band overlap in the gapless channel for one spin channel and small energy gap of 167 meV for other spin. A negative and linear out-of-plane magnetoresistance response was observed in these films. The temperature dependent anomalous Hall effect measurement gives nearly temperature independent carrier concentration (and/or) mobility with anomalous Hall conductivity of 91.35 S/cm at 5K. Also, the AHE transport is found to be majorly governed by momentum space driven Berry curvature. All these properties collectively imply that the grown film possesses disordered-SGS like behaviour. The result of the study suggests that CFCG is a potential candidate to be utilized in spintronics-based devices such as spin-injectors.

## सार

स्पिन गैपलेस सेमीकंडक्टर्स (SGSs) नया क्वांटम सामग्रियों का एक दिलचस्प वर्ग है जो एक स्पिन चैनल के लिए शून्य बैंड गैप और दूसरे स्पिन चैनल के लिए सेमीकंडक्टिंग बैंड गैप के साथ अपनी अजीब बैंड संरचना के कारण अर्धचालक और फेरोमैग्नेट के बीच अंतर को पाटता है। हेस्लर मिश्र धातुओं में एसजीएस विशेषताओं की उपस्थिति, विशेष रूप से सह-आधारित हेस्लर मिश्र धातुओं में, उनके उच्च क्यूरी तापमान ( $T_C$ ) और ट्यून करने योग्य इलेक्ट्रॉनिक और चुंबकीय संरचना के कारण और भी अधिक आशाजनक है; इसलिए वे पतला चुंबकीय अर्धचालक (DMS) के लिए उपयुक्त प्रतिस्थापन के रूप में कार्य कर सकते हैं। आजकल, 1:1:1:1 स्टोइकोमेट्री के साथ सह-आधारित इक्वेटोमिक क्वाटरनेरी हेस्लर मिश्र (EQHAs) बहुत अधिक फोकस में हैं क्योंकि छद्म टर्नरी मिश्र धातुओं की तुलना में उनमें उच्च स्पिन प्रसार लंबाई होती है। इनमें से कुछ यौगिकों ने कथित तौर पर एसजीएस जैसी विशेषताएं दिखाई हैं। इस थीसिस कार्य में, हमने दो सह-आधारित ईक्यूएचए पतली फिल्मों का विकास और अध्ययन किया है: CoFeMnSi (CFMS) और CoFeCrGa (CFCG)।

अध्ययन में संरचनात्मक, चुंबकीय और परिवहन गुण शामिल हैं। इन दो मिश्र धातुओं के अलावा, एक इंसुलेटिंग ऑक्साइड  $MgAl_2O_4$  (MAO) को भी MAO/CFMS/MAO हेटरोस्ट्रक्चर में लंबवत चुंबकीय अनिसोट्रॉपी (PMA) से संबंधित अध्ययन के लिए उगाया गया था और संरचनात्मक, चुंबकीय, रूपात्मक और स्पेक्ट्रोस्कोपी-आधारित अध्ययनों के लिए विशेषता थी। इन हेटरोस्ट्रक्चर में W और Ti सामग्रियों का उपयोग एक सुरक्षात्मक कैपिंग परत के रूप में किया गया था।

सबसे पहले, सीएफएमएस पतली फिल्म (~60 nm) के उच्च क्रम वाले चरण को सी (100) सबस्ट्रेट पर अनुकूलित किया गया था और विभिन्न संरचनात्मक, संरचनात्मक, चुंबकीय और परिवहन माप किए गए थे ताकि फिल्म की एसजीएस विशेषता का आकलन किया जा सके। प्रतिरोधकता के नकारात्मक तापमान गुणांक और लगभग तापमान स्वतंत्र वाहक एकाग्रता और गतिशीलता के साथ सीएफएमएस फिल्म का आदेशित चरण एसजीएस मानदंडों का पालन करने के लिए पाया गया।

चरण अनुकूलन और एसजीएस व्यवहार के सफल सत्यापन के बाद, अगले ही दिन हमने ~50 nm पतला CFMS नमूना विकसित किया है और विसंगतिपूर्ण हॉल प्रभाव (AHE) और कमजोर स्थानीयकरण (WL) घटना के लिए अध्ययन किया है। दो-वाहक मॉडल के माध्यम से अनुदैर्ध्य

चालकता डेटा की फिटिंग ने विकार फिल्म नमूने की उपस्थिति का सुझाव दिया। विभिन्न मॉडलों के माध्यम से विषम हॉल प्रतिरोधकता/चालकता की स्केलिंग ने उचित ठहराया कि सीएफएमएस में एचई मुख्य रूप से गति स्थान बेरी वक्रता के कारण एक आंतरिक बिखरने वाले तंत्र द्वारा नियंत्रित होता है। आंतरिक विसंगतिपूर्ण हॉल चालकता ( $\sigma_{AH}^{int}$ ) का प्रयोगात्मक मूल्य लगभग 37.75 एस/सेमी प्राप्त किया गया था, जो कि पूरी तरह से व्यवस्थित सीएफएमएस संरचना के लिए सैद्धांतिक रूप से अनुमानित मूल्य से काफी बड़ा पाया गया है और संभवतः सीएफएमएस फिल्म नमूने में मौजूद मौलिक विकार के कारण होता है। डब्लूएल व्यवहार को 1टी तक कम चुंबकीय क्षेत्र शासन में मैग्नेटोरेसिस्टेंस (एम आर) वक्रों में तेज नकारात्मक क्यूप्स की उपस्थिति से उचित ठहराया गया था। इसका आगे का औचित्य चरण सुसंगतता लंबाई, माध्य मुक्त पथ, प्रीफैक्टर और नमूना आकार के बीच अंतर-तुलना के माध्यम से किया जाता है। चरण सुसंगतता लंबाई और प्रीफैक्टर को हिकामी-लार्किन-नागोका (एच एल एन) मॉडल के माध्यम से चालकता सुधार वक्रों को फिट करके निकाला जाता है, इसका मतलब है कि मुक्त पथ वाहक एकाग्रता से प्राप्त होता है जिसका मूल्यांकन ए एच ई डेटा से किया जाता है और नमूना आकार फिल्म की मोटाई के रूप में लिया जाता है।

अगले अध्ययन में पीएमए को 300°C और 400°C पर रखे गए MAO/CFMS/MAO/Ti हेटरोस्ट्रक्चर में महसूस किया जाता है। हम दिखाते हैं कि इंटरफेशियल पीएमए एनीलिंग तापमान और सीएफएमएस परत की मोटाई ( $t_{CFMS}$ ) के प्रति बहुत संवेदनशील है।  $t_{CFMS} = 2.0$  nm के लिए एक बड़ा पीएमए हासिल किया जाता है। पीएमए के साथ आउट-ऑफ-प्लेन संतृप्ति चुंबकत्व में सुधार निचले एमएओ/सीएफएमएस इंटरफेस द्वारा उल्लेखनीय रूप से उत्तेजित पाया गया है। इसके अलावा, टीसीएफएमएस  $\leq 1.5$  एनएम के साथ जमा किए गए स्टैक के लिए एक अक्षीय पीएमए देखा जाता है। 400°C पर एनीलिंग ने हेटरोस्ट्रक्चर की बेहतर तापीय स्थिरता के साथ पर्याप्त इंटरफेशियल ऑक्सीकरण को महत्वपूर्ण रूप से बढ़ावा दिया। एक्स-रे फोटोइलेक्ट्रॉन स्पेक्ट्रोस्कोपी के माध्यम से, MAO के साथ CFMS द्वारा साझा किए गए इंटरफेस पर Co-3d<sup>2</sup> और O-2p<sub>z</sub> ऑर्बिटल्स के संकरण के परिणामस्वरूप होने वाले Co-O बांड के गठन को इन स्टैक्स में देखे गए PMA की सूक्ष्म उत्पत्ति के रूप में पहचाना जाता है। इन निष्कर्षों से संकेत मिलता है कि सीएफएमएस और एमएओ-आधारित संरचनाओं में अगली पीढ़ी के स्पिट्रॉनिक उपकरणों के लिए अपार संभावनाएं हैं।

पीएमए के अध्ययन को MAO/CFMS/MAO/W स्टैक में पीएमए की जांच करके आगे बढ़ाया गया है। जब MAO परतों ( $t_{MAO}$ ) की मोटाई 1.5 nm है, तो अधिकतम प्रभावी PMA ऊर्जा घनत्व ( $K_{eff}$ )

$\approx 2.48 \times 10^6$  erg/cc देखा जाता है। सीएफएमएस और एमएओ मोटाई को ट्यून करते समय पर्याप्त इंटरफेशियल ऑक्सीकरण स्थिति के कारण एमएओ/सीएफएमएस और सीएफएमएस/एमएओ इंटरफेस में संरचनात्मक परिवर्तनों से पीएमए और संतृप्ति चुंबकत्व ( $M_s$ ) का विकास काफी प्रेरित होता है। अध्ययन से पता चलता है कि निकटवर्ती इंटरफेस में ऑक्सीजन प्रसार को नियंत्रित करना विशिष्ट चुंबकीय गुणों को प्राप्त करने का एक आसान साधन हो सकता है। ये परिणाम पीएमए को नियोजित करने वाले उपन्यास स्पिंट्रॉनिक उपकरणों की प्राप्ति की दिशा में एक नया रास्ता खोलते हैं।

अंत में, हमने उद्योग-व्यवहार्य मैग्नेट्रोन स्पटरिंग तकनीक का उपयोग करके सी (100) सबस्ट्रेट पर विकसित एक अनुकूलित CoFeCrGa हेस्लर मिश्र धातु पतली फिल्म ( $\sim 50$ nm) पर विभिन्न संरचनात्मक, चुंबकीय और परिवहन माप किए हैं। विकसित फिल्म ने  $1.86 \mu_B/f.u$  के संतृप्त चुंबकीयकरण के साथ एक्स-रे विवर्तन माप स्थितियों के दिए गए सेट के तहत A2-ऑर्डरिंग दिखाई। (5K पर) और क्यूरी तापमान  $\sim 595$ K। नकारात्मक तापमान गुणांक के साथ लगभग रैखिक रूप से भिन्न अनुदैर्घ्य प्रतिरोधकता देखी गई। "दो-वाहक मॉडल" के माध्यम से फिट किया गया अनुदैर्घ्य चालकता वक्र एक स्पिन चैनल के लिए गैपलेस चैनल में मामूली बैंड ओवरलैप और अन्य स्पिन के लिए  $167$  meV का छोटा ऊर्जा अंतर देता है। इन फिल्मों में एक नकारात्मक और रैखिक आउट-ऑफ-प्लेन मैग्नेटोरेसिस्टेंस प्रतिक्रिया देखी गई। तापमान पर निर्भर विषम हॉल प्रभाव माप 5K पर  $91.35$  S/cm की विषम हॉल चालकता के साथ लगभग तापमान स्वतंत्र वाहक एकाग्रता (और/या) गतिशीलता देता है। इसके अलावा, एएचई परिवहन को प्रमुख रूप से गति अंतरिक्ष संचालित बेरी वक्रता द्वारा नियंत्रित पाया जाता है। ये सभी गुण सामूहिक रूप से दर्शाते हैं कि विकसित फिल्म में अव्यवस्थित-एसजीएस जैसा व्यवहार है। अध्ययन के परिणाम से पता चलता है कि सीएफसीजी स्पिन-इंजेक्टर जैसे स्पिंट्रॉनिक्स-आधारित उपकरणों में उपयोग किए जाने वाला एक संभावित उम्मीदवार है।

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