Research Article

Journal of Environmental Nanotechnology

Adaptation and Optimization of Space_GMR Technique: A Novel *In-Situ* Method for Simultaneous Growth of Single Crystals and Thin Films – A First Time New Feasibility Study

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Received: 20.01.2018 Accepted: 20.03.2018

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ABSTRACT

Development of a novel in-situ method for simultaneous growth of single crystals and thin films of material. Material (Chromium doped Gallium Zinc Oxide) (CGZO) to be grown as metal – (Indium) (In) incorporated single crystal, and the thin film was taken as a precursor and put into a bath containing acid as a reaction speed-up reagent (catalyst) as well as a solvent with metal as cation scavenger. By this novel method, Cr: IGZO crystals having trigonal, tetragonal, pentagonal and hexagonal facets and thin films having polycrystalline nature were prepared from a single optimized bath. Properties of both crystals and thin films were going to be studied using an X-ray diffractometer (XRD) and Energy Dispersive Analysis by X-rays (EDAX). Combinations of ZnO were well-known wide bandgap compound semiconductors, ceramics, optomechanical and used as anti-thermal coatings in aerospace vehicles. Thus a space_gmr technique was found to be a new low cost and advantageous method for in-situ and simultaneous growth of single crystals and thin films of material.

Keywords: Crystals; In-situ; NEMS;Tertiary; Thin Films**.**

1. INTRODUCTION

Production of a material with high perfection is essential for the future progress of science and technology. Recently both crystal growth and thin film deposition were matched together as twin brothers of the art of material growth and two pillars of the advanced scientific world (Punarja *et al*. 2015). They play an important role in material processing, including advanced Nano-Electronics and nano-Machining System technology (NEMS). There are too many methods for crystal growth and thin films, such as Liquid Encapsulated Czochralski (LEC) pulling technique and Molecular Beam Epitaxy (MBE) technique (Zachary *et al.* 2015 *)*. In this work, we have developed an in-situ new, low cost, advantageous growth method for single crystals and thin films (Boatner *et al*. 2013; Galazka *et al*. 2013). A material that we have grown as single crystals and thin films from a single optimized bath using this method is (Chromium doped Gallium Zinc Oxide) (CGZO) incorporated Indium (In), i.e., Cr: IGZO is widely used as a ceramic material.

2. EXPERIMENTAL PROCESSES

Material (Chromium doped Gallium Zinc Oxide) (CGZO) to be grown as metal-(Indium) (In) incorporated single crystal and the thin film was taken as a precursor and put into a neutral bath containing acid as a reaction speed-up reagent (catalyst) as well as a solvent with metal as cation scavenger.

2.1 Chemical bath preparation

Johnson-Mathey 'specpure' grade Chromium doped Gallium Zinc Oxide (CGZO) was selected as suitable material to be grown as metal-(Indium) (In) incorporated single crystal and thin film. Then we put it into a bath containing highly pure nitric acid and sulfuric acid as suitable solvents as well as reaction catalysts. Optimization of the present work was carried out with variation in parameters such as i. acid concentration (10 ml, 15 ml, 20 ml, 30 ml, 40 ml, 50 ml), ii. Precursor concentration (2.5 g, 5 g, 10 g, 15 g, 20 g, 30 g) iii. Metal concentration (0.25 g, 0.5 g, 0.75 g, 1 g, 1.5 g, 2 g) iv. Time of thin-film deposition (T_d) (1 day, 2 days, 3 days, 4 days, 5 days, 6 days) v. time of crystal growth evaporation (T_e) (5 days, 10 days, 15 days, 20 days, 25 days, 30 days). In this way, we have prepared various saturated baths (for simultaneous growth of Cr:IGZO single crystals and thin films), and they were kept in a BOROSIL glass beaker at room temperature in an unstirred condition in 6 trials. Indium was chosen as the related cation (NO_3^- ion and SO_4^- ion) scavenger. Afterwards, hot chromic acid-treated glass substrates (cleaned with trichloroethylene, methanol and

acetone) were immediately dipped into the freshly prepared bath. In general, properly treated substrates provides a catalyzed surfaces for uniform deposition.

The resultant solution baths were allowed to evaporate in a cleanroom environment. Observations were made at frequent intervals in order to monitor the crystal growth and thin film deposition. Average growth and harvest time vary from 20 days and 150 hrs respectively for single crystals and thin films throughout this work. As a result, Cr: IGZO single crystals and thin films were formed. After gently harvesting, we have just dried the single crystals at ordinary room temperature (Chetan *et al*. 2013). Thin films on substrates were annealed at 250 ^{o}C for 15 min. For our naked eye observation and through microscope view, we have confirmed the perfection of the grown thin films and crystals, respectively. The faceted (trigonal, tetragonal, pentagonal and hexagonal) crystals showed high-quality optimization perfection. The grown crystals and thin films (size: 1 cm x 1 cm) were sent for structural and compositional characterization by using a Philips X-pert – MPD x-ray diffractometer and a Philips ESEM-TMP+EDAX energy dispersive x-ray analyzer. The results were awaited and will be discussed later. Thin-film itself is a polycrystalline nature (Faceted trigonal, tetragonal, pentagonal and hexagonal structures confirmed the single-crystalline nature of the crystals, as well as the crystals, contain a major amount of ZnO. Pale yellow, Yellowish orange and brown colors confirmed that the crystals contain a major amount of chromium. The metallic coloring of crystals confirmed the contents of Indium and Gallium.

3. RESULTS AND DISCUSSION

3.1 Surface morphological – micro-structural characterization

By adopting the harvested single crystals from the optimization baths to Labomed® microscopic view, we have gathered much more inferences about the faceted nature of the crystals. Fig.1. Explains preliminary origination of spurious crystallization, finally leads to facet unit cells of Cr: IGZO crystals. Fig. 2 Implies the growth of unit cells towards bigger size built up of Cr: IGZO single crystals, via coagulation of unit cells. Fig.3. Enumerates the coagulated unit cells lead to crude from of faceted Cr: IGZO single crystals, via stacking of hexagonal, pentagonal, tetragonal, trigonal lattices. Also, Optimized conditions for getting triangle faced crystals that obtained from the optimization process as refined results were Acid concentration (AC): 15 ml, Precursor concentration : (CGZO): 5 grams, Metal concentration : (In): 0.5 gram, Time of thin-film deposition (T_d) : 2 days and Time of crystal growth evaporation : (T_e) : 5 days. Fig.4 Illustrates the intermediate Cr : IGZO single crystal from crude forums. Tetragonal, pentagonal and hexagonal single crystals were well clearly shown in the above image.

Table 1. Optimized conditions to obtain tetra, Penta and hexagonal crystals

Tetra	Penta	Hexa
AC: 20 ml	AC : 40 ml	AC : 50 ml
CGZO : 15 gm	CGZO : 20 gm	CGZO : 30 gm
In : 1 gm	In : 1.5 gm	In : 2 gm
T_d : 4 days	T_d : 4 days	T_d : 6days
T_e : 10 days	T_e : 15 days	T_e : 20 days

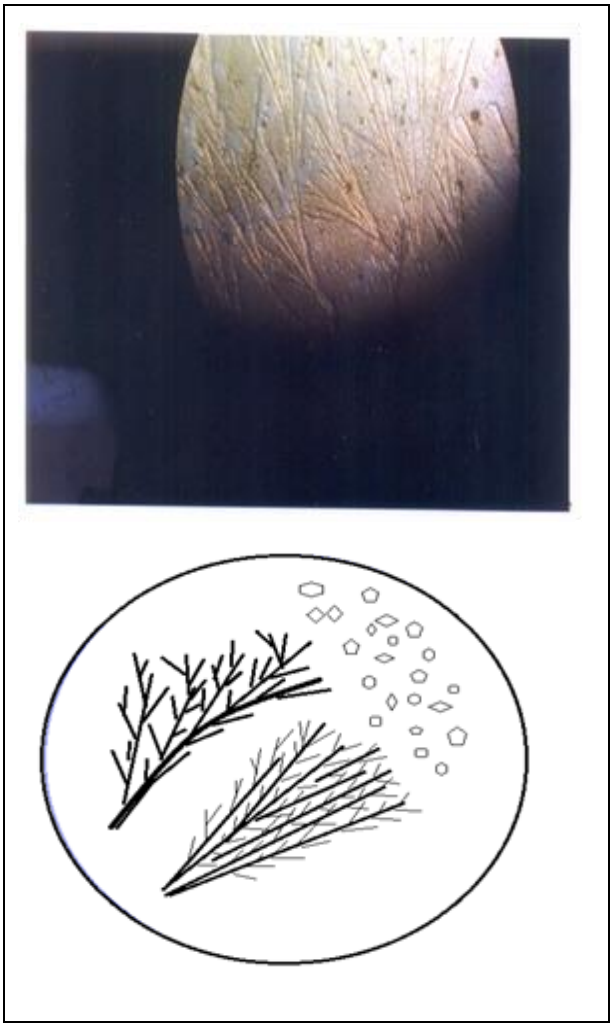

Fig. 1: Explains preliminary origination of spurious crystallization, finally leads to facet unit cells of Cr: IGZO crystals

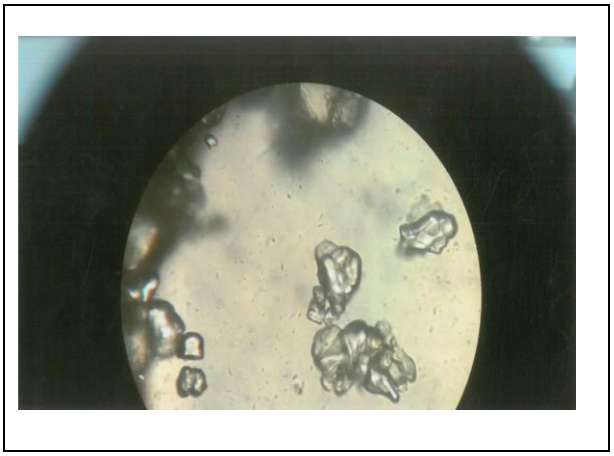

Fig. 2: Implies the growth of unit cells towards bigger size built up of Cr: IGZO single crystals, via coagulation of unit cells

Fig. 3: Enumerates the coagulated unit cells lead to crude from of faceted Cr: IGZO single crystals., via stacking of hexagonal, pentagonal, tetragonal, trigonal lattices

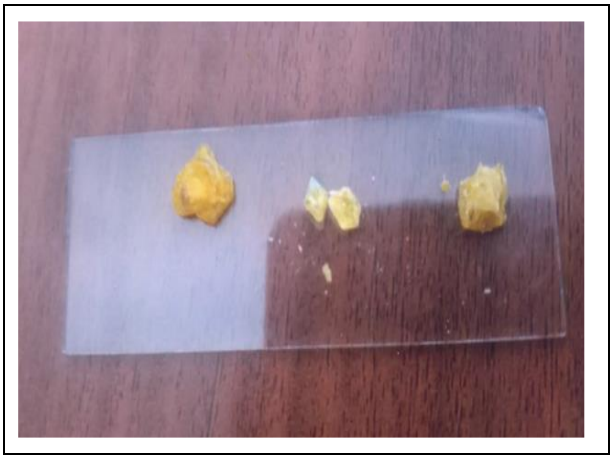

Fig. 4: Illustrates the intermediate Cr : IGZO single crystal from crude forums. Tetragonal, pentagonal and hexagonal single crystal were well clearly shown in the above image

Fig.5. Depicted the final matured growth of pentagonal Cr: IGZO single crystal. The stacking of pentagonal layers was well clearly shown. Fig.6. Edge pattern of a Cr: IGZO single crystal which joining two faces. Fig.7. Illustrates the stacking of hexagonal layers one by one. Fig.8. The stacking of tetragonal layers of unit cells shows the evidence for crystal growth in such a way that the remaining portion of the entire crystal is the repetition of the previously originated unit cells.

Fig.9. Shows the edge pattern of joining two faces of a Cr: IGZO single crystal. Fig.10. Depicted the stacking layers of tetragonal faceted single crystals. Fig.11. Illustrates the stacking of hexagonal layers of a perfectly grown Cr : IGZO single crystal.

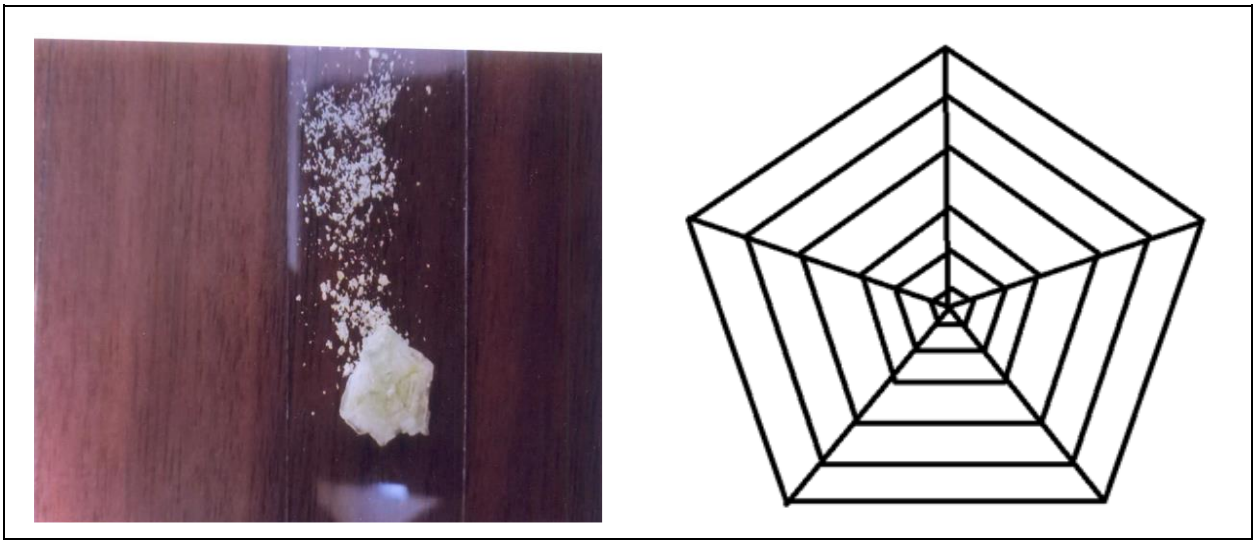

Fig. 5: a) Depicted the final matured growth of pentagonal Cr: IGZO single crystal. The stacking of pentagonal layers was well clearly shown. b) Schematic diagram of fig. 5a

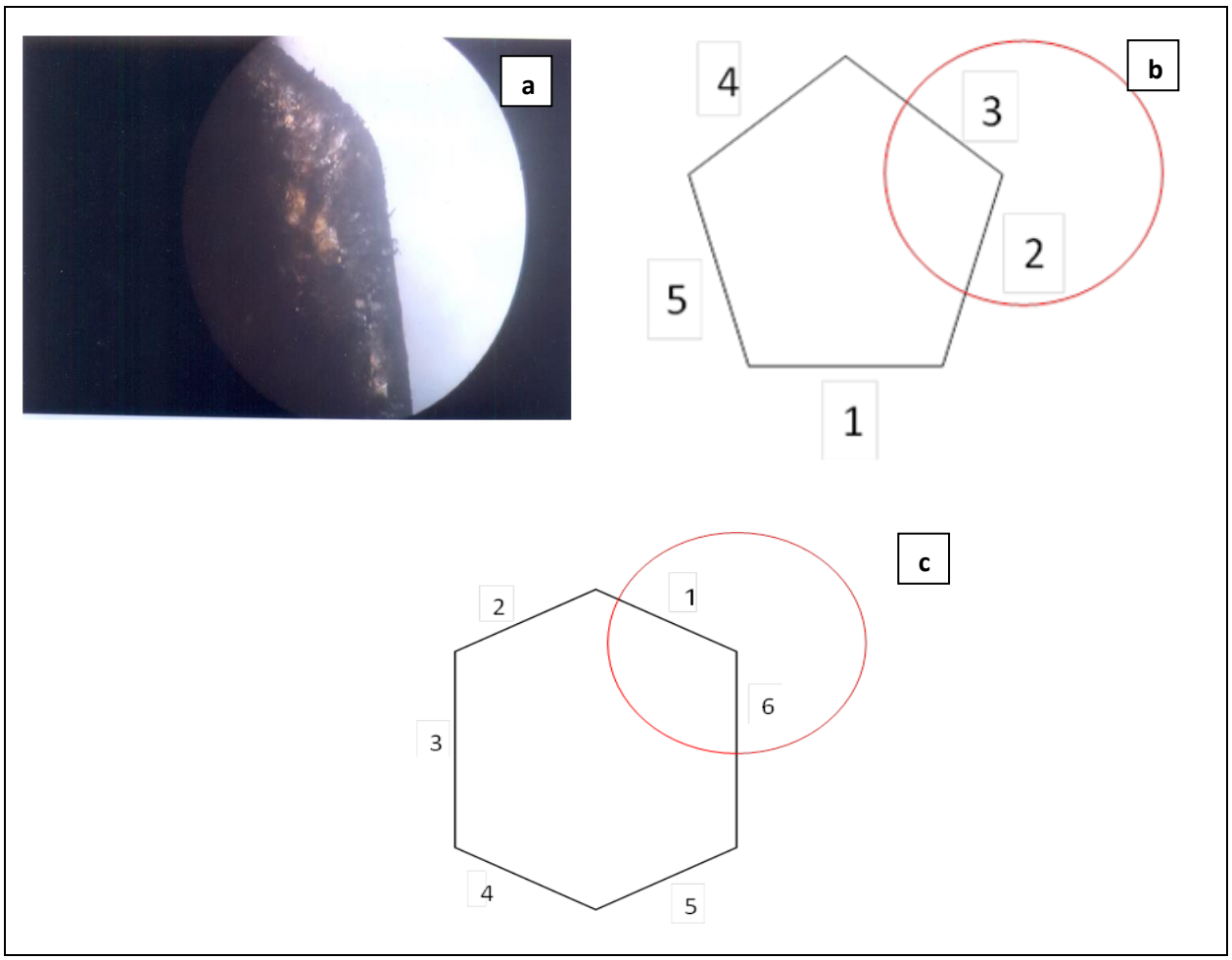

Fig. 6: a) Edge pattern of a Cr: IGZO single crystal which joining two faces b) & c) Schematic diagrams of fig 6a

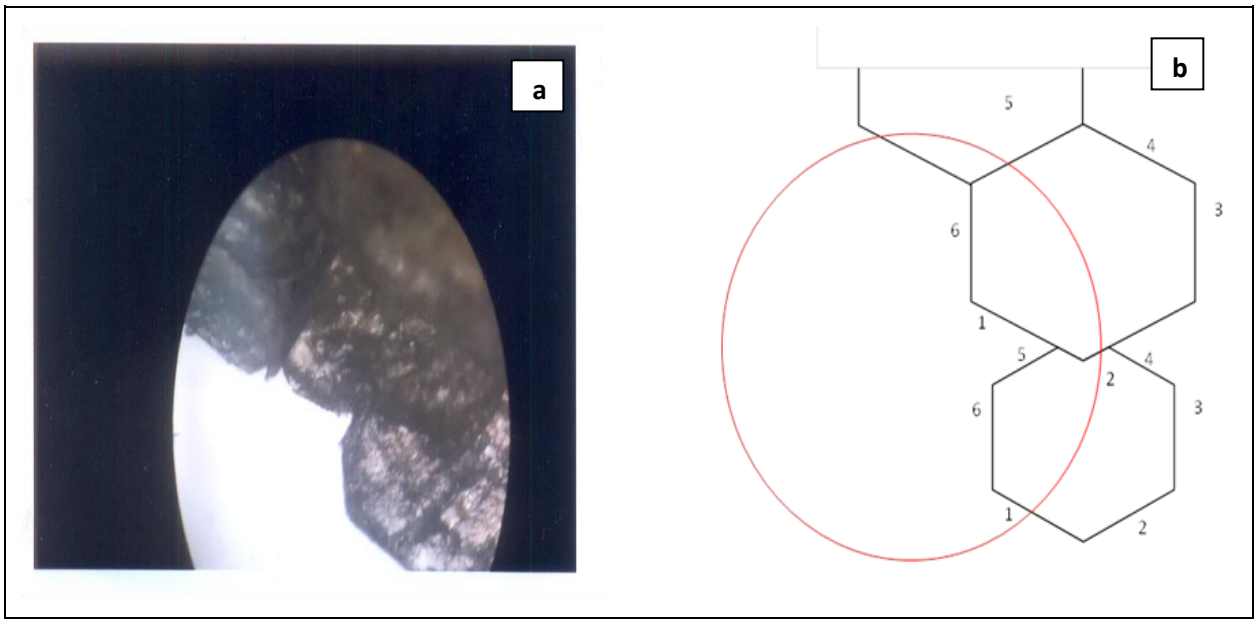

Fig. 7: a) Illustrates the stacking of hexagonal layers one by one b) Schematic diagrams of fig. 7a

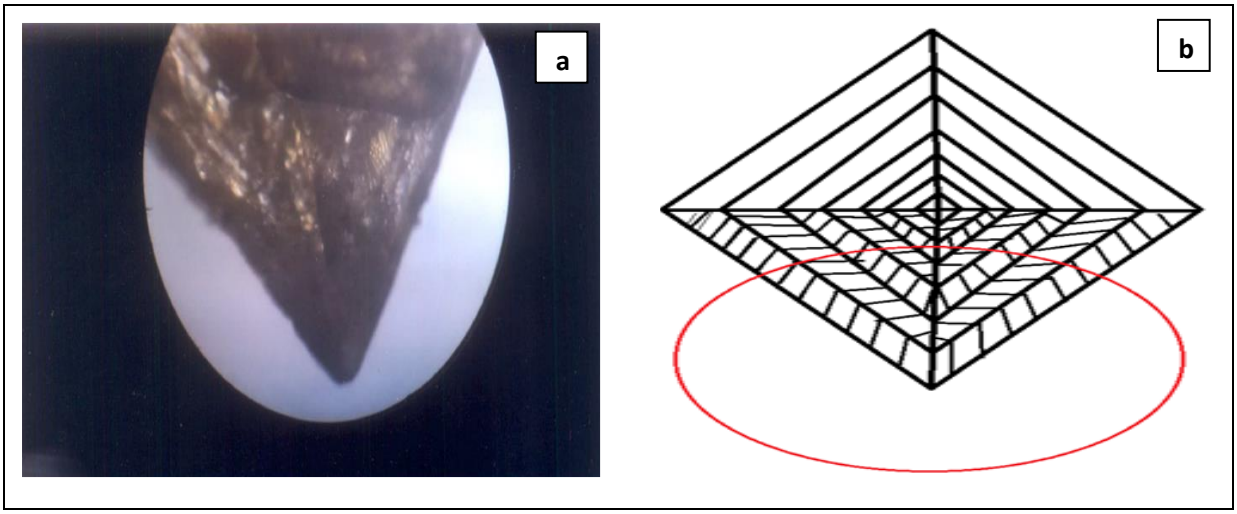

Fig. 8: Stacking of tetragonal layers of unit cells shows the evidence for crystal growth in such a way that the remaining portion of the entire crystal is the repetition of the previously originated unit cells b) Schematic diagram of fig. 8a

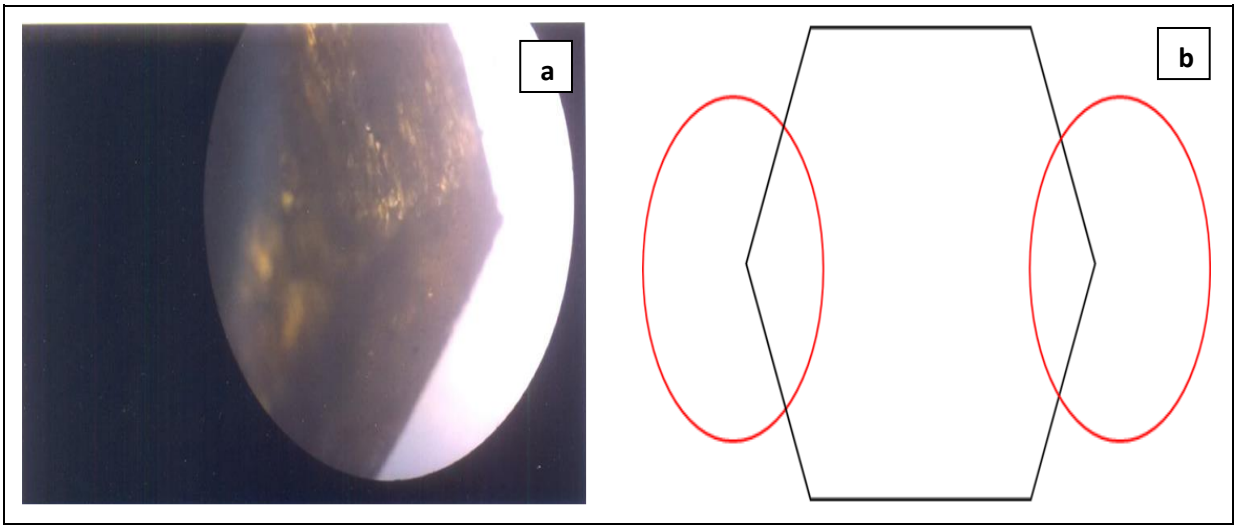

Fig. 9: a) Shows the edge pattern of joining two faces of a Cr: IGZO single-crystal b) Schematic diagram of fig. 9b

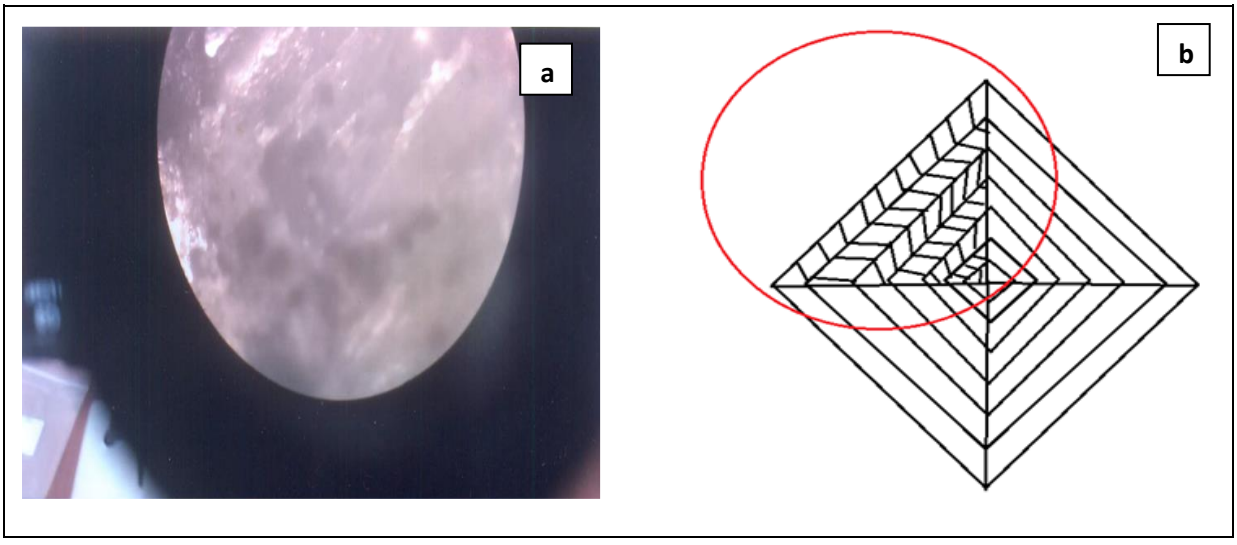

Fig. 10: a) Depicted the stacking layers of tetragonal faceted single crystals b) Schematic diagram of fig. 10a

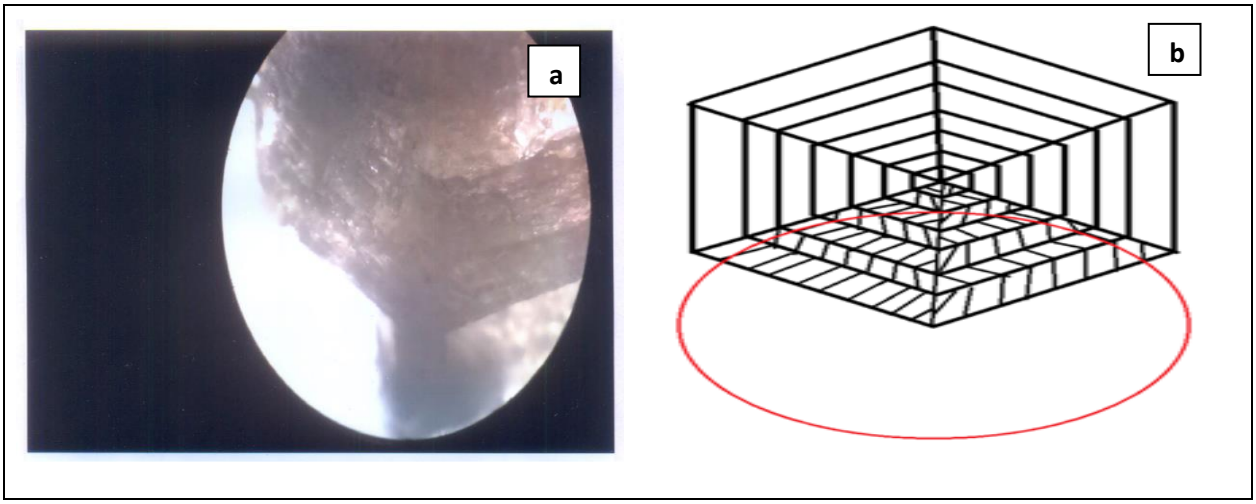

Fig. 11: a) Illustrates the stacking of hexagonal layers of a perfectly grown Cr : IGZO single crystal b) Schematic diagram of fig. 11a

3.2 Compositional characterization – EDAX Analysis

From the compositional characterization (dispersive energy analysis by x-rays),the followinginferences were gathered from the results of optimized samples. Generally, we have observed that the emerged peaks of O, In, Zn, Ga, and Cr indicated and confirmed that the crystal (material) contains a major amount of the respective elements. Also, the material was constructed by these elements. Thus from the EDAX spectrum, we confirmed that the material is Cr doped IGZO combination. The contents of Si, Na and Mg were due to the fact that it was included in the material due to solvent etching on the surface of the glassy beaker. The dominant peak of Sulphur is due to the inclusion of sulphuric acid as a solvent.

Fig. 12.a – Fig. 15.a implies the compositional analysis of thin films and single-crystal prepared at various optimized conditions.

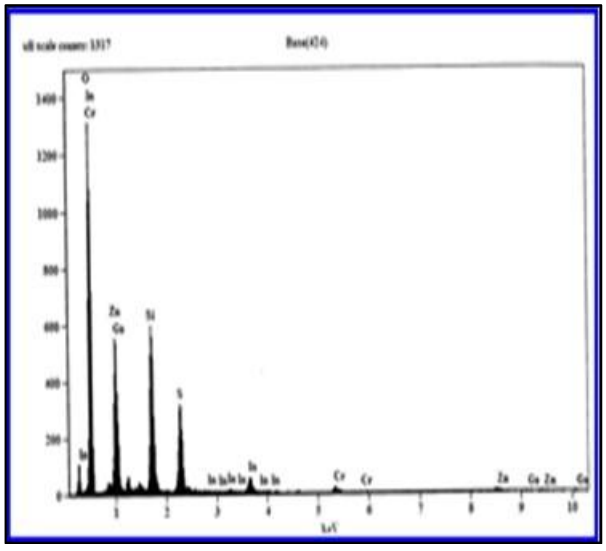

Fig. 12a: Illustrates the EDAX compositional spectrum of Cr: IGZO thin film prepared at optimized condition : Acid concentration (AC) : 15 ml , Precursor concentration : (CGZO): 5 grams , Metal concentration : (In): 0.5 gram , Time of thin film deposition (T_d) : 2 days and Time of crystal growth evaporation : (T_e) : 5 days

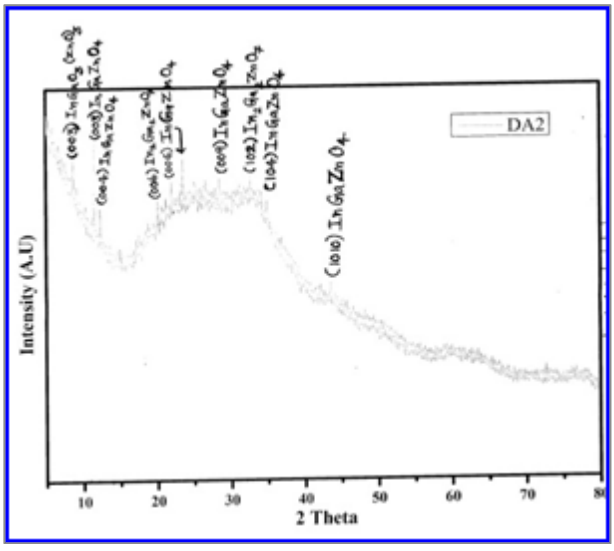

Fig. 12b: Illustrates the X-ray Diffractogram of a Cr: IGZO thin film prepared at optimized condition : Acid concentration (AC) : 15 ml , Precursor concentration : (CGZO): 5 grams , Metal concentration : (In): 0.5 gram , Time of thin film deposition (T_d) : 2 days and Time of crystal growth evaporation : (T_e) : 5 days

3.3 Structural characterization – X-ray diffraction studies

From the x-ray diffraction studies, generally, we have observed that irregular pattern of various (h,k,l) indices confirmed the polycrystalline nature of the grown thin films (Didi *et al*. 2014; Wong *et al*. 2014). Also, the repeated, regular pattern of 1st order and 2nd order diffraction peaks confirmed the single-crystalline nature of the crystal. Also, the diffraction spectrums confirmed that the material is IGZO combination compounds. The unmarked peaks were due to chromium oxide phases. The amorphous background is due to glass substrates on which thin films were deposited. The prominent peaks illustrated that the secret the major quantity of lattices were grown along that particular direction. Fig. 12.b – Fig. 15.b picture the structural characterization of thin films and single-crystal prepared at various optimized conditions.

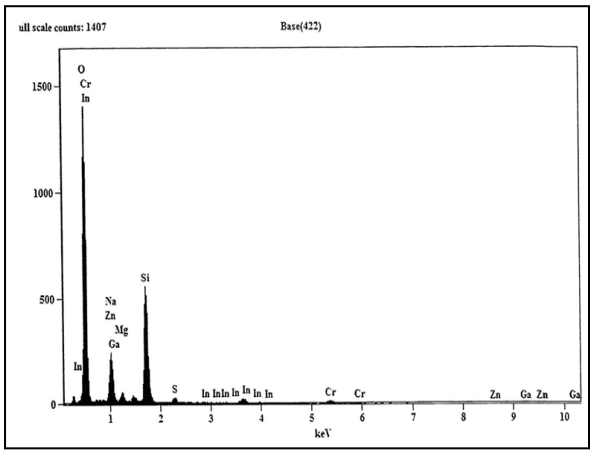

Fig. 13 a: Illustrates the EDAX compositional spectrum of a Cr: IGZO thin film prepared at the optimized condition: Acid concentration (AC) : 20 ml, Precursor concentration : (CGZO): 15 grams , Metal concentration : (In): 1 gram , Time of thin-film deposition (T_d) : 4 days and Time of crystal growth evaporation : (T_e) : 10 days

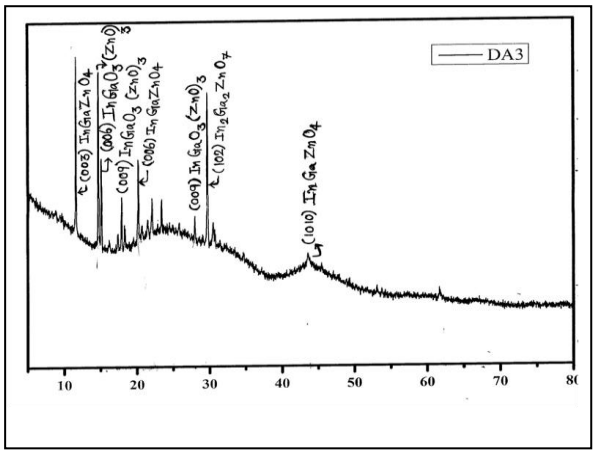

Fig. 13 b: Illustrates the X-ray Diffractogram of a Cr: IGZO thin film prepared at the optimized condition : Acid concentration (AC) : 20 ml , Precursor concentration : (CGZO): 15 grams , Metal concentration : (In): 1 gram , Time of thin-film deposition (T_d) : 4 days and Time of crystal growth evaporation : (T_e) : 10 days

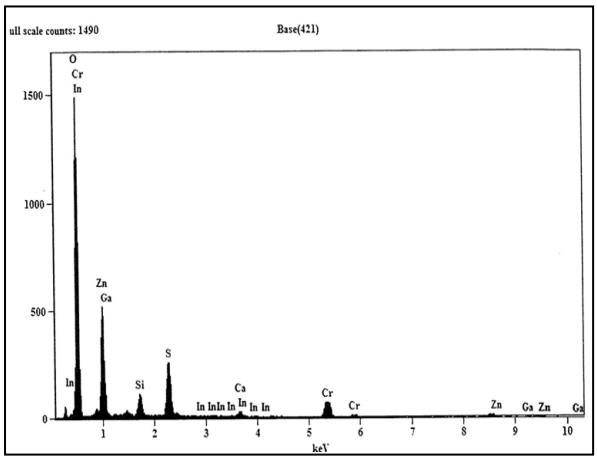

Fig. 14a: Illustrates the EDAX compositional spectrum of a Cr: IGZO thin film prepared at the optimized condition: Acid concentration (AC): 40 ml, Precursor concentration : (CGZO): 20 grams, Metal concentration : (In): 1.5 grams, Time of thin-film deposition (T_d): 4 days and Time of crystal growth evaporation : (T_e): 15 days

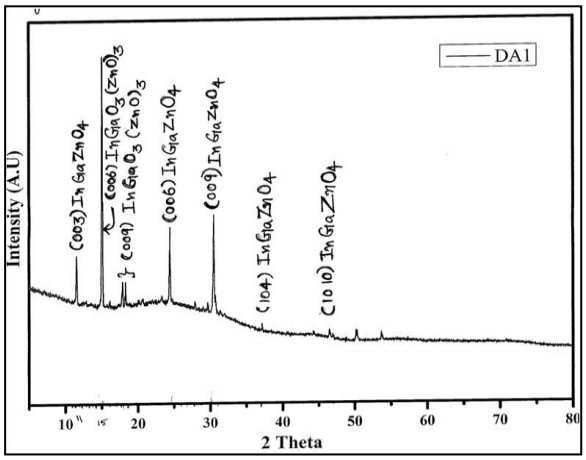

Fig. 14b: Illustrates the X-ray Diffractogram of a Cr: IGZO thin film prepared at the optimized condition : Acid concentration (AC) : 40 ml , Precursor concentration : (CGZO): 20 grams , Metal concentration : (In): 1.5 grams , Time of thin-film deposition (T_d) : 4 days and Time of crystal growth evaporation : (T_e) : 15 days

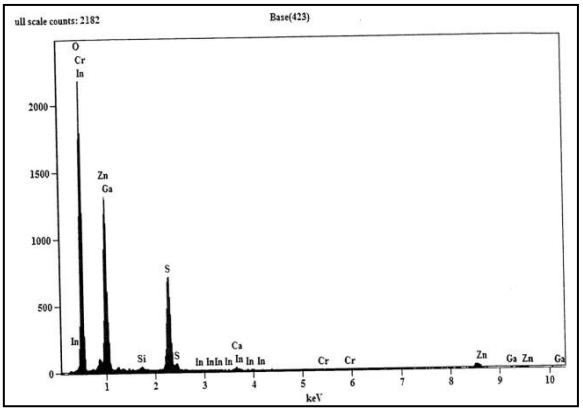

Fig. 15a: Illustrates the EDAX compositional spectrum of a Cr: IGZO hexagonal faceted single crystal prepared at the optimized condition : Acid concentration (AC) : 50 ml , Precursor concentration : (CGZO): 30 grams , Metal concentration : (In): 2 grams , Time of thin-film deposition (T_d) : 6 days and Time of crystal growth evaporation : (T_e) : 20 days

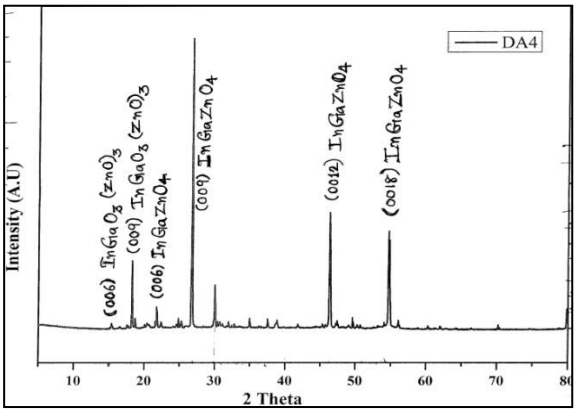

Fig. 15b: Illustrates the X-ray Diffractogram of a Cr: IGZO hexagonal faceted single crystal prepared at the optimized condition : Acid concentration (AC) : 50 ml , Precursor concentration : (CGZO): 30 grams , Metal concentration : (In): 2 grams , Time of thin-film deposition (T_d) : 6 days and Time of crystal growth evaporation : (T_e) : 20 days

Optimized condition for getting triangle faced crystals

1. Acid concentration (AC) : 15 ml
2. Precursor concentration : (CGZO): 5 grams
3. Metal concentration : (In): 0.5 gram
4. Time of thin film deposition (Td) : 2 days
5. Crystal growth evaporation time: (Te):5 days

Table 2. Optimized conditions to obtain tetra, Penta and hexagonal crystals

Tetra	Penta	Hexa
AC: 20 ml	AC : 40 ml	AC : 50 ml
CGZO : 15 gm	CGZO : 20 gm	CGZO : 30 gm
In : 1 grams	In : 1.5 grams	In : 2 grams
T_d : 4 days	T_d : 4 days	T_d : 6days
T_e : 10 days	T_e : 15 days	T_e : 20 days

5. CONCLUSION

According to the best of our knowledge, this is the first time that high crystalline quality single crystals and thin films of material were obtained from a single source using an *in-situ* method. Spontaneous room-temperature growth of Cr: IGZO single crystals and thin films with well defined faceted morphology was emphasized and developed. Thus space_gmr technique was found to be a new, low cost and advantageous method for *in-situ* and simultaneous growth of single crystals and thin films of material. We hope that these data may be helpful either as a scientific or technical basis in material processing.

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