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Article

Resolving the problem of thin films crystallinity at ambient temperature by oriented magnetic fields

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ABSTRACT Grazing incidence X-Ray Diffraction spectroscopy was employed to characterize crystallinity of Iron, Nickel, Copper and Tungsten, prepared by sparking discharge process in presence of 0.4 T magnetic field at ambient temperature 25◦C. Iron thin film preserved crystallinity even after one year of ageing. Nickel exhibit higher crystallinity when sparked in nitrogen gas flow from the one sparked in oxygen. Tungsten was successfully crystalized after just 40 minutes of sparking inside of magnetic field.

KEYWORDS crystallization of thin films; ambient crystallization; room temperature crystallization; magnet induce crystallization; sparking discharge

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Significance Statement

The relation between deposition temperature and thin film quality is crucial for properties, potential application and mass production of nanomaterials. By decreasing annealing temperature, we can design environmental-friendly and energy efficient way for thin film fabrication. Describing reactions in external magnetic and electric ordered field, help us understand new mechanism of kinetic and physical processes involved in nucleation and crystallization. Conducting in air atmosphere, as oppose of water medium, we are able to get a new insight in DOLLOP theory of magnetic field influence, developed by JMD Coey et al.

As thinner as can get, thin film will require higher thermal condition to crystalize,[1,2,3] thus if it is combined in nanocomposite material or deposited on substrate material that is not able to sustain high temperatures it represents a dead end for scaling up or any wide range commercialization's[4,5]. In material chemistry field, low temperature is considered below 600 degrees of Celsius[6]. Ambient temperature research will open new door for facile approach that can provide a cost-effective synthesis that will allow integration of thin film on temperature sensitive and provide alternative for widely used thermal annealing. In fabrication of Ti_2O thin films, for now water vapor and UV induced crystallization are used as the strategies for crystallization of thin films[7,8,9] Room temperature heating free growth and crystallization of perovskite films[10] in ambient air without use of thermal annealing was reported first by Dubey et al. in which exposure of thin film to humid air (40% RH) promoted crystallization. Radiofrequency plasma[11] (RF) treatment developed by Osaki et al were used to crystalize ITO and Ti2O thin films that were prepared on PET substrate by DC magnetron sputtering method[12]. Miniemulsion (ME) technique was used by Gross group to obtain nanocrystaline CuS[13]. In our research group, we use thin films for application in photovoltaics, self-

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cleaning glass coating, anti-dust coating, thermochromic, sensors, antibacterial and hydrophobic coting as well as air purifier. If crystallinity is needed for any of application thermal annealing is required, the temperature applied will depend on film thickness and material composition. Bretos et al.[14] (2018) in a review of low-temperature crystallization point out the crystallization process as a limiting step in the low- temperature processing of metal oxide thin film materials. As one of strategies to achieve crystallization apart from photochemistry previously mentioned, authors discussed on the so-called seeding effect and excess metal addition. There is no mention of ambient (room-temperature) reactions, also authors exclusively focus on wet routes. In our research of room temperature crystallization of metal thin films, we employed breaking voltage discharge across tips of metal wires, that way electric current across the gap between tips of wires, will induce ablation, evaporation and ionization of metal (Al, Fe, Ni, Cu, W). We observe how magnetic field strength of 0.4T affect deposition time on substrate and crystallinity of thin film, we also present result of one-year Fe iron thin film aging by exposure to atmospheric condition as conducted in our previous work.[15] Our primary objective was to examine time needed to achieve crystallization of thin films at 0.4 Tesla. Various metals are used in this study, however we failed to achieve any crystallization of aluminum under Nitrogen, Argon or Oxygen flow. After 12h of sparking there were no visible peaks on XRD. In contrast Tungsten, paramagnetic metal exhibited crystallization after 45 minutes in ambient atmosphere, corresponding to peak intensity achieve with annealing at 400 degrees as reported previously. [20,21] *Figure 1* represent following W phases a) higher peak W_3O (00-041-1230) b) smaller peak. on 45 degrees represent beta W (03-065-6453). Result present at *Figure 1* of magnetic field influence at tungsten crystallization in ambient conditions for 40 minutes is counterintuitive, knowing that W has highest melting and boiling point, we can explain also oxidation of W as other authors did on preparation of W and W_3O thin films, they observed that a low oxidized tungsten phase exists from beginning of thin film growth.[22] However, W_3O phase higher intensity from pure W implies it is likely related to tungsten target cleaning[23], which was not done in present experiment. We can only with certainty conclude that atmospheric oxygen was not integrated into thin film trough vaporization/ionization reaction. The integration of oxygen and nitrogen was previously reported on example where zerovalent iron starting material was used. These thin films preserved crystallinity even after one year of exposure to ambient conditions as represented at Figure 2. Another ferromagnetic material, that crystalized in 30 minutes of sparking was Nickel. We also compared possibility of sparked Nickel to incorporate nitrogen. In nitrogen flow, at 0.4 T, following phases were detected Ni3N (01-070-9598) and pure zerovalent Nickel phase (03-065-0380). Mixed phase nickel based thin films are important for water splitting applications[25] and environmental applications[26]. Figure 3 represent GIXRD results of Nickle wire sparked inside of nitrogen flow and 0.4T. XRD peaks intensity decreased if Nickel was ionised inside of atmospheric air. It is possible to observe preserved zerovalent nickel (03-065-2865) and NiN (01-083-8042), NiO (00-047-1049). Influence of gas flow type on nanoparticle morphology by spark discharge was described already by Schmid-Otto research group which produce aerosols by sparking method.[27] Diamagnetic material that we use for sparking inside of nitrogen flow and 0.4 T field was Copper. We were surprised with results of crystallization and phase involving nitrides occurred during XRD analysis. Time for thin film fabrication was 30 minutes, phases represented at Figure 4, include pure Cu phase (03-065-9743) and CuN (01-076-8854). This can be explained as magnetic field influence on ions or vaporized zerovalent metal and it creates mixture of radicals where they can enter reaction if radicals are in close proximity of each other. Radical pairs are formed between Copper and excited nitrogen. Nitrogen is ionized by applying voltage trough spark gap. Only by looking at this system as chemical, we can explain why aluminum didn't crystalize because by ionization with spark discharge, two valence electron that successfully pair inside of magnetic field, and thus opposes the change that produced magnetic field. Table 1 represent valence electrons of materials used in this study. In K. Watanabe et al., book[28] the first use of magnetic field applied for crystal growth process was for damping convection in semiconductor melts. They review crystallization of organic molecules and proteins, in ambient condition, this method is beneficial due to possibility of protein denaturation at higher temperature from 40°C, therefor they examined crystallization of proteins at 0T, 5T and 11 T field. Magnetic field influenced

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the nucleation process, the ratio of the growth rates of the crystal faces. It was noticed that those tendencies in magnetic field are enhanced by increasing protein concentration. Also, by increasing magnetic field, number of crystals were decreased. According to them, crystallization of protein occurred while they were sedimenting from solution. They conclude that number of crystals oriented with magnetic field, can be increased by using higher concentration of protein and taller cells (crystals grown from taller cells). It was found that a magnetic field decreased the growth rate of the crystals in an electrolyte solution. Regarding inorganic molecules, there are two direction examining effect of magnetic field on crystallization, one in thermal processing/analysis[29] and other in solution chemistry[30] (sedimentation experiments). In first case, the high magnetic field (up to 20T) was introduced in high temperature environments in order to control material functionality. Two reasons for this: A) effect on phase transitions and B) an increase in coercivity of permanent magnets. Iron phase in multicomponent crystalline alloys will increase in the nucleation rate Fe by annealing in magnetic fields. On the other side, in solution chemistry, precipitation of 90% of $CaCO^3$ in 1.2 T external magnetic field resulted in sedimentation of aragonite/vaterite crystals. externally applied magnetic field is lowering the zeta potential of $CaCO_3$.[31] Aragonite is formed at high temperature and pressure from melts. Therefore, the formation of calcite is energetically in favor than of aragonite. However, why in applied external field, aragonite is formed over calcite? Theoretically this can happen only if magnetic field is 45T, but still researchers achieve it under application of 0.4T high gain of aragonite concentration is achieved. (80%)[30] Chandrasekhar[32] used 5.5 T field on magnetic on sodium hexafluorosilicate to improve the crystallinity. They explain effect referring to Mitrovic[33,34,35] observation, that Lorentz force influence on ion movement in solution as they pass through magnetic field and slowing down the growth disrupting the regularity of the lattice. Mitrovic[35] who conducted synthesis of manganese chloride and Rochelle salt in presence of magnetic field and Ohagaki[36] et al. who investigated barium chloride and produced crystals under magnetic field, at ambient and temperature of maximum saturation of solution ($50^{o}C$), according to their findings every molecule or ion is regarded as diamagnet and orientation is results of movement and alignment of those diamagnets. H.E. Lundager Madsen[37], precipitated at 0,27T ($25^{o}C$) and found an effect of the magnetic field on carbonates and phosphates with diamagnetic metal ions. In 2008, Tai et al,[31] will induce crystallization of $CaCO_3$ in pipes using 0.0074 T. They confirmed that aragonite crystals are formed and calcite growth is inhibited in magnetic field. Permanent magnets outside of steel pipes were 0.1T strong, generating the field inside of pipes, due to Teflon coating, of a 74 gauss. This utilization of weak magnetic force or field is currently finding applications in environmental technology as enhancing absorption and removal of heavy metals and other pollutants[38-42]By now, we can observe two directions in research of magnetic field application for chemical reaction. One group that use field above 5T for crystallization of alloy melts[43-47] and groups addressing electrolyte crystallization in magnetic field.[48,49] J.M.D. Coey and H.E.L. Madsen, assumed role of water and prenucleation clusters, referred as DOLLOPs. Proton dimers will mix single-triplet change in ionic bond of salts that crystalized under magnetic fields. Why these authors are so vividly focused on water molecules and protons, it appears to be related to historical context. Namely, at that time, there was controversial trend of magnetic treatment water.[50] Researchers never explored possibility that water is just a medium for magnetic field, magnetic field influence on ions outside of solutions. As seen with magnetic spattering method that was used to increase the density of argon ion plasma, in most of cases chemical reactions such as oxidation and nitridification were not desirable, so effect on chemical reaction of magnetron was suppress in describing about magnetic field ordered reactions, even though this technique is famous and appeared at the same amount time as crystallization of solutions in presence of magnetic field.[51] This is perfectly understandable due to lack of interdisciplinarity at that time and different purpose of both methods. Sparking process is perfect combination for establishing conditions of ionization without solvents and obtaining experimental condition in which chemical reaction can be influenced by magnetic field without complex apparatuses that magnetron require. We would explain crystallization of thin films in magnetic fields by effect of ground vs exited state of metals and valence electrons ordering. These two approaches were deducted from formation of metal ions in liquids and alloys,[52] and size of atom/ion/molecule

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effect.[53] Aluminum belongs to boron group, which have three electrons in last orbital with valence configuration ns^2np^1. Since we sparked aluminum wire, therefor ionized with breakdown voltage atoms in it, we assumed that electron from p-shell was loss, positive ionization and that magnetic field couldn't interact with other paired electrons. In order to prove this hypothesis, we decided to spark Indium wire in magnetic field. Unfortunately, we achieved crystallization of indium, as showed at Figure 5, we obtained two peaks of different intensity, the first one is measurement at the center of magnet, where field is homogeneous, and second 3mm from center, at Figure 5b with blue dot is marked central position of substrate, ring pattern appears due to rotation of magnet and substrate on it. Quality assurance of process was comparatively done by sparking of tin(II) oxide (SnO) and preparation of tungsten (W) that will cover whole substrate (as recommended by Rigaku) prepared without presence of magnetic field, with furnace annealing. We didn't obtain any crystallization from SnO and W-covered substrate. We obtained crystallization at 0.4 Tesla, of iron, nickel, copper, indium, tungsten. These elements are different in terms of atomic number, density, melting points, atomic orbitals and magnetic properties of elements. We provided evidence that crystallization is achievable outside of water and that previous hypothesis of proton transfer is not suitable for explanation of crystallization.

All thin films are prepared at ambient condition, which could possibly open the door for integration with polymer processing and wearable materials that are sensitive to increased temperature. Also, whole process is breakthrough in energy efficient synthesis. Most important contribution is elucidating effects on crystal formation, as alternative vision of the one claimed by Coey and other explanation of magnetic field effect.[54] Returning to magnetocrystalline anisotropy as a future scope of magnetic field ordering is essential for understanding magnetic field effect on ordering of ionized metal ions and other molecules.

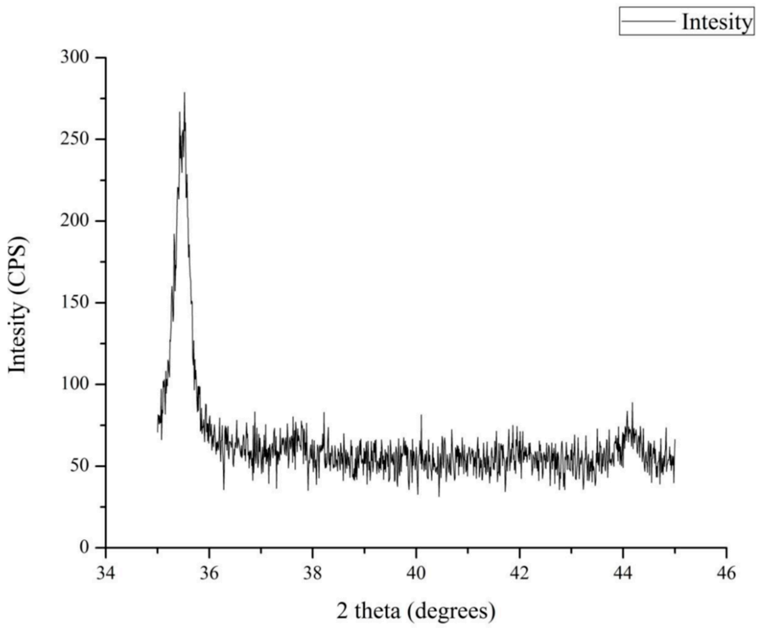

Figure 1. "Tungsten (W) peaks of GIXRD.".

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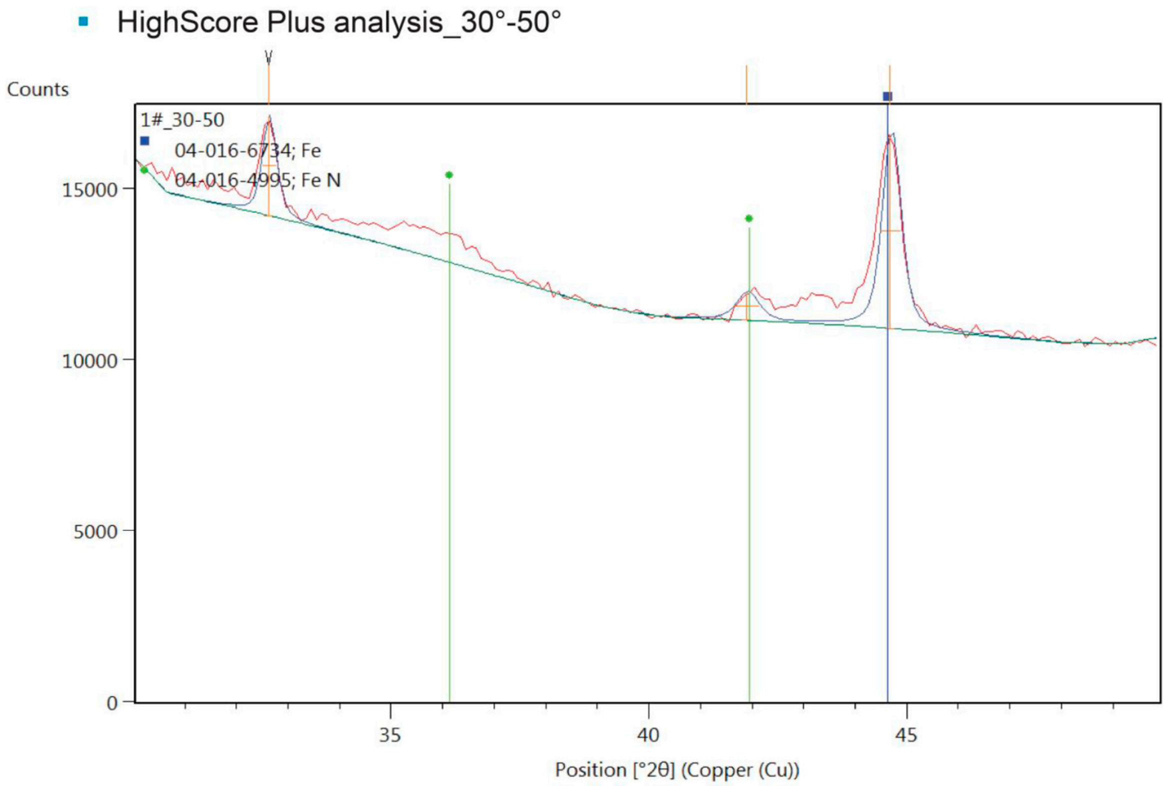

Figure 2. “GIXRD HighScopre Plus PanAnalytical analysis of iron nitride thin films, exposed to air for one year, prepared by sparking method”.

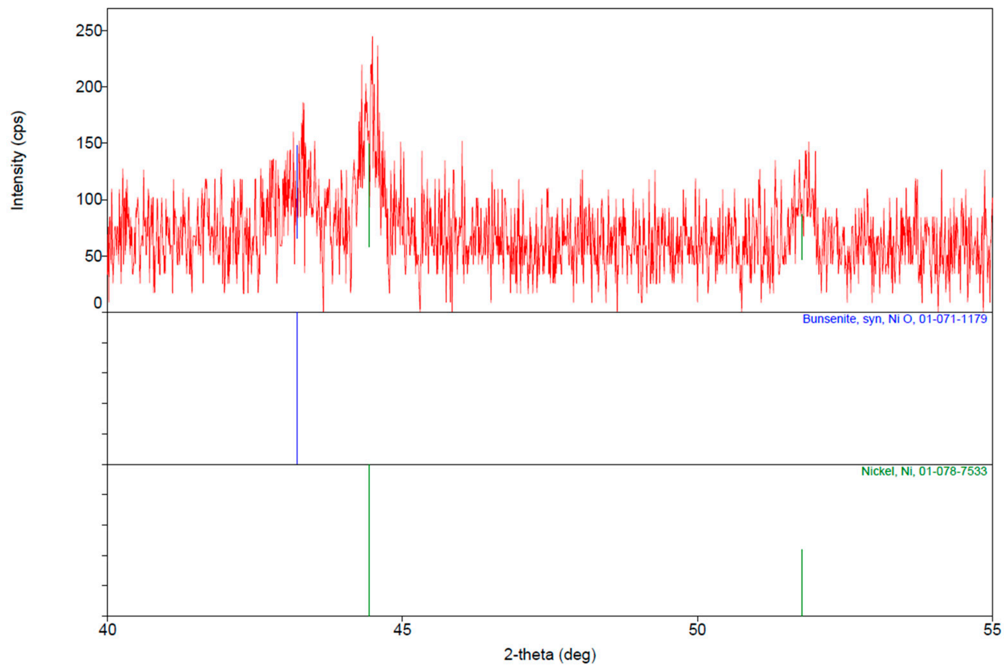

Figure 3. “Nickel GIXRD results, sparked in nitrogen for 30 minutes. Bunsenite phase coincidence with nitride phase.”.

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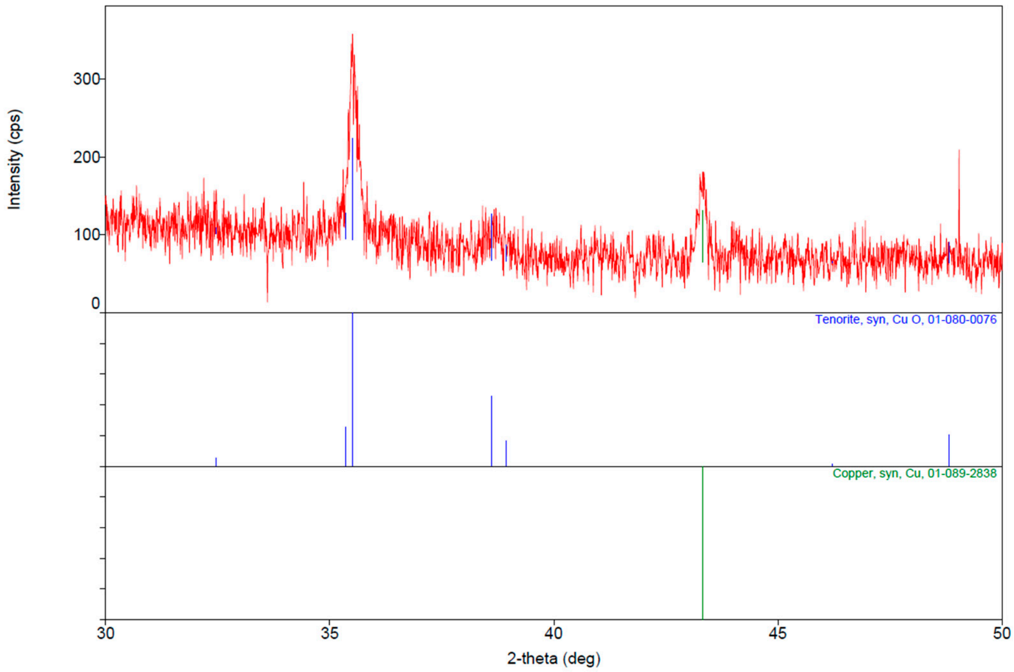

Figure 4. "Copper wire sparked inside of nitrogen flow. GIXRD results of Cu thin films".

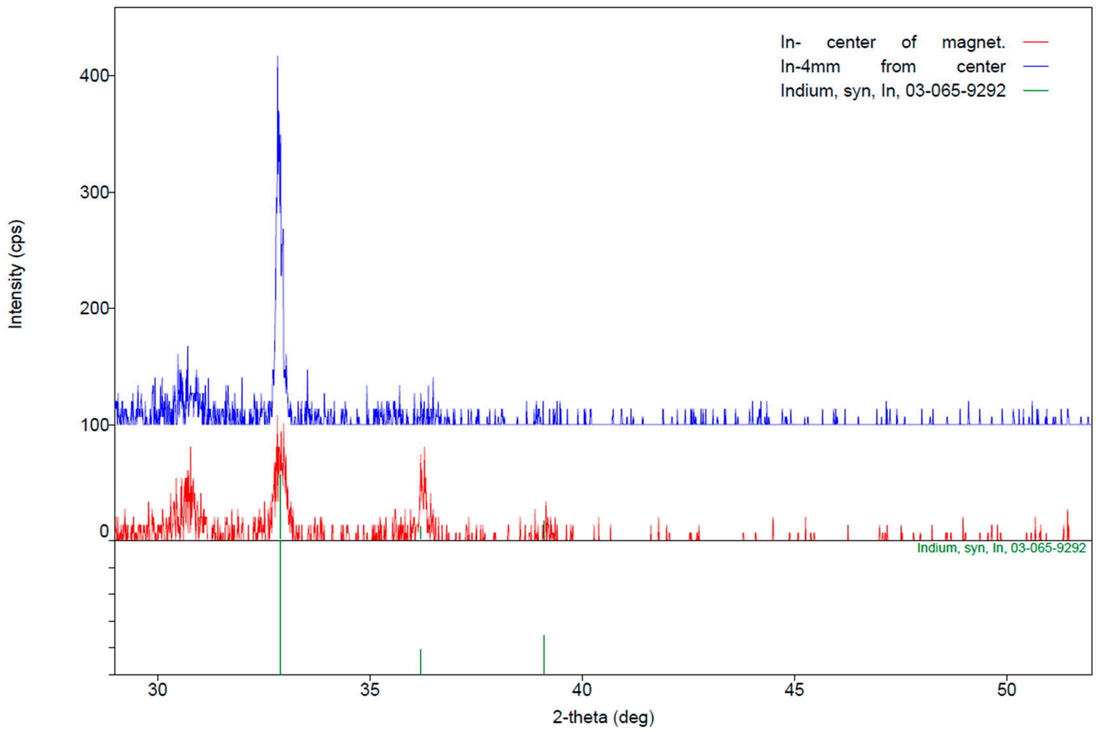

Figure 5. "Indium wire sparked inside of nitrogen flow, at 0.4 T. Blue-GIXRD results from center, Red-4mm from center, as depicted at Figure 5b.".

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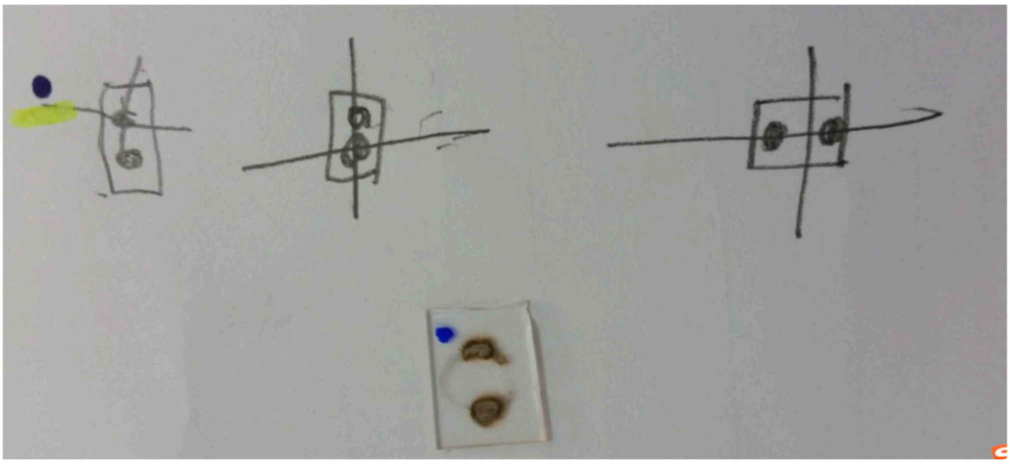

Figure 5b. "Picture of quartz substrate with indium thin film, blue dot depicted position of center. Graphical representation of 3 GIXRD measurements.".

Experimental Methods

Metal wires purchased from ADVENT research materials, ltd. Iron, aluminum, Tungsten, Copper, Nickel 0.50 mm diameter wire of 99.5% and Indium wire of 99.9% purity that were annealed in clean conditions. Catalogue number FE525711, CU514511, AL501012, W557609, NI535311, IN522109.Quartz substrate used for deposition of nanoparticles onto sur- face. 0.4 Tesla high temperature Neodymium magnet from Ningbo Risheng Magnets Co., Ltd. For thin film characterization, Rigaku Smartlab XRD with Rigaku's PDXL software for X-ray analysis was used. Cu source (1.541862 A) with D/teX Ultra 250 detectors. HighScore with the Plus option from PanAnalytical was used for Iron thin film characterization after one-year exposure.[24] *Sparking discharge method*. Metal nanoparticles were prepared as described previously[15 16 17 18 19]. In brief, on changeable ends of electronic circuit, metal wires purchased from ADVET were placed, 2 mm in distance of each other and 1 mm from quartz substrate. Circuit consists of power supply that is connected to 7KV Boost Step-up Power Module High-voltage Generator Transformer (Note: generator is commercial name, in scientific context it should be noted that this is converter) that leads current to the capacitor. Four metallic fire on two parallel circuit, two for each, are ending with interchangeable heads, where metal wires are inserted. Beneath substrate, magnet is placed on rotating motor. Rotation is used to examine influence that different position of substrate in magnetic field have in crystallinity and Magnetic strength measure with magnetometer to be set at 0.4T. These ends of circuit are placed in flow box where pressure and gas flow can be controlled.

TABLES.

"**Table 1.** Sparked materials in this research, valence electrons".

Element	Atomic number	Valence electrons	Density g/cm^3	Melting point °C
Al	13	[Ne]$3s^2$ $3p^1$	2,70	660
Fe	26	[Ar] $3d^6$ $4s^2$	7,86	1535
Ni	28	[Ar] $3d^8$ $4s^2$	8,908	1453
Cu	29	[Ar]$3d^{10}4s^1$	8,96	1085
In	49	[Kr] $4d^{10}5s^2 5p^1$	7,31	156,6
Tin oxide	molecule	Sn = O	6,95	1630
W	74	[Xe] $4f^{14}5d^4 6s^2$	19,25	3422

Source: National Institute of Standards and Technology; nist.gov

The authors declare no competing financial interests.

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REFERENCES

1. Zhang, QM.; Xu, H.; Fang, F.; Cheng, ZY.; Xia, F.; You, H. Critical Thickness of Crystallization and Discontinuous Change in Ferroelectric Behavior with Thickness in Ferroelectric Polymer Thin Films. *Journal of Applied Physics* **2001**, 89, 2613-2616.
2. Chen, RQ.; Lu, QQ.; Cheng, QD.; Ao. LB.; Zhang, CY.; Hou, H.; Liu, YM.; Li, DW. Yin, DC. An ignored variable: solution preparation temperature in protein crystallization. *Scientific reports* **2015**, 5, 7797-7782. DOI: 10.1038/srep07797
3. Ferri, FA.; Low-temperature metal-induced Crystallization of Mn-containing Amorphous Ge Thin Films., *Journal of Non-Crystalline Solids* **2012**, 358, 58– 60.
4. Regula, M.; Ballif, C.; Remškar, M.; Lévy, F. Crystallinity and Texture Promotion in WS2 Thin Films., *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films* **1997**, 15, 2323–2329.
5. Pellegren, J.P.; and Sokalski, V. M., Thickness and Interface-Dependent Crystallization of CoFeB Alloy Thin Films., *IEEE Transactions on Magnetics* **2015**, 51, 1–3. DOI: 10.1109/TMAG.2015.2435798
6. Yoon, SY.; Kim, KH.; Kim, CO.; Oh, JY.; Jang, J. Low temperature metal induced crystallization of amorphous silicon using a Ni solution. *Journal of applied physics* **1997**, 82, 5865–5867.
7. JohnáK, A. et al., Rapid Room Temperature Crystallization of TiO2 Nanotubes, *CrystEngComm* **2017**, 19, 1585–1589.
8. Su, J.; Zou, X.; Li, B.; Chen, H.; Li, X.; Yu, Q.; Mi, Q.; Chen, J.S. Accelerated Room-temperature Crystallization of Ultrahigh-surface-area Porous Anatase Titania by Storing Photogenerated Electrons. *Chemical Communications* **2017**, 53, 1619–1621.
9. Lamberti, A.; Chiodoni, A.; Shahzad, N.; Bianco, S.; Quaglio, M.; Pirri, C.F., Ultrafast Room-temperature Crystallization of TiO2 Nanotubes Exploiting Water-vapor Treatment, *Scientific reports* **2015**, 5, 7808-7814. DOI: 10.1038/srep07808
10. Dubey, A.; Kantack, N.; Adhikari, N.; Reza, K.M.; Venkatesan, S.; Kumar, M.; Khatiwada, D.; Darling, S.; Qiao, Q., Room Temperature, Air Crystallized Perovskite Film for High Performance Solar Cells. *Journal of Materials Chemistry A* **2016**, 4, 10231–10240.
11. Ohsaki, H.; Shibayama, Y.; Suzuki, M.; Kinbara, A.; Yashiro, H.; Watanabe, T., Room Temperature Crystallization by RF Plasma., *Thin Solid Films* **2008**, 516, 4490–4494.
12. Ohsaki, H.; Suzuki, M.; Shibayama, Y.; Kinbara, A.; Watanabe, T.; Room Temperature Crystallization of Indium Tin Oxide Films on Glass and Polyethylene Terephthalate Substrates Using RF Plasma. *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films* **2007**, 25, 1052–1055. https://doi.org/10.1116/1.2748807
13. Morgese, G.; Dolcet, P.; Feis, A.; Gellini, C.; Gialanella, S.; Speghini, A.; Badocco, D.; Pastore, P.; Casarin, M.; Gross, S. Room-Temperature Crystallization of CuS Nanostructures for Photothermal Applications through a Nanoreactor Approach., *European Journal of Inorganic Chemistry* **2017**, 20, 2745–2754. DOI: 10.1002/ejic.201601435
14. Bretos, I.; Jiménez, R.; Ricote, J.; Calzada, M.L.; Low-temperature Crystallization of Solution-derived Metal Oxide Thin Films Assisted by Chemical Processes., *Chemical Society Reviews* **2018**, 47, 291-308.
15. Stefan, R., Jakmunee, J., Punyodom, W. and Singjai, P., A Novel Strategy for Longevity Prolongation of Iron-based Nanoparticle Thin Films by Applied Magnetic Force. *New Journal of Chemistry* **2018**, 42, 4807-4810. DOI 10.1039/C7NJ04730D
16. Kumpika, T.; Thongsuwan, W.; Singjai, P., Optical and Electrical Properties of ZnO Nanoparticle Thin Films Deposited on Quartz by Sparking Process. *Thin Solid Films* **2008**, 516, 5640–5644.
17. Chuminjak, Y., Daothong, S., Kuntarug, A., Phokharatkul, D., Horprathum, M., Wisitsoraat, A., Tuantranont, A., Jakmunee, J.; Singjai, P., High-performance Electrochemical Energy Storage Electrodes Based on Nickel Oxide-coated Nickel Foam Prepared by Sparking Method., *Electrochimica Acta* **2017**, 238, 298–309.
18. Chuminjak, Y., Daothong, S., Reanpang, P., Mensing, J.P., Phokharatkul, D., Jakmunee, J., Wisitsoraat, A., Tuantranont, A.; Singjai, P., Electrochemical energy-storage Performances of Nickel Oxide Films Prepared by a Sparking., *RSC Advances* **2015**, 5, 67795–67802.

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Peer-reviewed version available at *Crystals* **2018**, *8*, 362; doi:10.3390/cryst8090362

19. Meuller, B.O.; Messing, M.E.; Engberg, D.L.; Jansson, A.M.; Johansson, L.I.; Norlén, S.M.; Tureson, N.; Deppert, K., Review of spark discharge generators for production of nanoparticle aerosols., *Aerosol Science and Technology* **2012**, 46, 1256-1270.
20. Christou, K.; Louloudakis, D.; Vernardou, D.; Savvakis, C.; Katsarakis, N.; Koudoumas, E.; Kiriakidis, G. Effect of solution chemistry on the characteristics of hydrothermally grown WO3 for electroactive applications. *Thin Solid Films* **2015**, 594, 333–337.
21. Vernardou, D.; Psifis, K.; Louloudakis, D.; Papadimitropoulos, G.; Davazoglou, D.; Katsarakis, N.; Koudoumas, E., Low pressure CVD of electrochromic WO3 at 400 C, *Journal of The Electrochemical Society* **2015**, 162, H579–H582.
22. Maillé, L.; Sant, C.; Le Paven-Thivet, C.; Legrand-Buscema, C.; Garnier, P. Structure and morphological study of nanometer W and W3O thin films. *Thin Solid Films* **2003**, 428, 237–241.
23. Girault, B.; Eyidi, D.; Goudeau, P.; Sauvage, T.; Guerin, P.; Bourhis, E.L.; Renault, P.O. Controlled Nanostructuration of Polycrystalline Tungsten Thin Films. *Journal of Applied Physics* **2013**, 113, 174310.
24. Degen, T.; Sadki, M.; Bron, E.; König, U.; Nénert, G. The HighScore suite., *Powder Diffraction* **2014**, 29, S13-S18. doi:10.1017/S0885715614000840
25. Shalom, M., Ressnig, D., Yang, X., Clavel, G., Fellinger, T.P. and Antonietti, M., Nickel Nitride as an Efficient Electrocatalyst for Water Splitting. *Journal of Materials Chemistry A* **2015**, 3, 8171-8177.
26. Rudd, P.A., Liu, S., Gagliardi, L., Young Jr, V.G. and Lu, C.C., Metal–Alane Adducts With Zero-Valent Nickel, Cobalt, and Iron. *Journal of the American Chemical Society* **2011**, 133, 20724-207273.
27. Feng, J., Guo, X., Ramlawi, N., Pfeiffer, T.V., Geutjens, R., Basak, S., Nirschl, H., Biskos, G., Zandbergen, H.W. and Schmidt-Ott, A. Green Manufacturing of Metallic Nanoparticles: a Facile and Universal Approach to Scaling Up. *Journal of Materials Chemistry A* **2016**, 4, 11222-11227.
28. Watanabe K., Motokawa, M. Eds.; Materials Science in Static High Magnetic Fields. Springer-Verlag, Berlin Heidelberg; 2002;
29. Onodera, R.; Kimura, S.; Watanabe, K.; Lee, S.; Yokoyama, Y.; Makino, A.; Koyama, K.; Magnetic Field Effects on Crystallization of Iron-based Amorphous Alloys., *Materials Transactions* **2013**, 54, 188-191.
30. Cefalas, A.C.; Kobe, S.; Dražic, G.; Sarantopoulou, E.; Kollia, Z.; Stražišar, J.; Meden, A. Nanocrystallization of CaCO3 at solid/liquid interfaces in magnetic field: A quantum approach. *Applied Surface Science* **2008**, 254, 6715–6724.
31. Tai, C.Y.; Wu, C.K.; Chang, M.C. Effects of Magnetic Field on the Crystallization of CaCO3 Using Permanent Magnets. Chemical Engineering Science 2008, 63, 5606 – 5612.
32. Chandrasekhar, R., Influence of Magnetic Field on Sodium Hexafluorosilicate Synthesis., *Journal of Crystal Growth* **2000**, 216, 407-412.
33. Mitrović, M.M., Growth Rate Dispersion of Small MnCl2· 4H2O Crystals II. Growth in a Magnetic Field. *Journal of Crystal Growth* **1991**, 112, 171-182.
34. Mitrović, M.M.; Ristić, R.I.; Ćirić, I. The Influence of a Magnetic Field on the Mosaic Spread and Growth Rate of Small Rochelle Salt Crystals. *Applied Physics A* **1990**, 51, 374-378.
35. Mitrović, M.M.; Žižić, B.B.; Napijalo, M.L.; Influence of Magnetic Field on Growth Rate Dispersion of Small Rochelle Salt Crystals. *Journal of Crystal Growth* **1988**, 87, 439—445.
36. Ohgaki, K.; Makihara, Y.; Sangawa, H., Effect of Exposure to Magnetism on Crystals Produced in Aqueous Solutions. *Chemical Engineering Science* **1994**, 49, 911-913.
37. Madsen, H.L.; Influence of Magnetic Field on the Precipitation of Some Inorganic Salts. *Journal of Crystal Growth* **1995**, 152, 94-100.
38. Fan, P.; Jiang, X.; Qiao, J.; Li, L. Enhanced Removal of Heavy Metals by Zerovalent Iron in Designed Magnetic Reactors. *Environmental Technology* **2017**, 1-9. doi: 10.1080/09593330.2017.1360398
39. Liang, L.; Guan, X.; Shi, Z.; Li, J.; Wu, Y.; Tratnyek, P. G. Coupled Effects of Aging and Weak Magnetic Fields on Sequestration of Selenite by Zero-Valent Iron. *Environmental Science & Technology* **2014**, 48, 6326-6334.
40. Xu, C.; Zhang, B.; Zhu, L., Lin, S.; Sun, X.; Jiang, Z.; Tratnyek, P. G. Sequestration of Antimonite by Zerovalent Iron: Using Weak Magnetic Field Effects to Enhance Performance and Characterize Reaction Mechanisms. *Environmental Science & Technology* **2016**, 50, 1483-1491.
41. Fan, P.; Sun, Y.; Qiao, J.; Lo I. M.; Guan, X. Influence of Weak Magnetic Field and Tartrate on the Oxidation and Sequestration of Sb (III) by Zerovalent Iron: Batch and Semi-Continuous Flow Study. *Journal of Hazardous Materials* **2018**, 343, 266-275.

42. Li, J.; Qin, H.; Zhang, W. X.; Shi, Z.; Zhao, D.; Guan, X. Enhanced Cr (VI) Removal by Zero-Valent Iron Coupled with Weak Magnetic Field: Role of Magnetic Gradient Force. *Separation and Purification Technology* **2017**, 176, 40-47.
43. Saban, K. V.; Jini, T.; Varghese, G. Influence of Magnetic Field on the Growth and Properties of Calcium Tartrate Crystals. *Journal of Magnetism and Magnetic Materials* **2003**, 265, 296-304.
44. Sazaki, G.; Durbin, S. D.; Miyashita, S.; Ujihara, T.; Nakajima, K.; Motokawa, M.; Magnetic Damping of the Temperature-Driven Convection in NaCl Aqueous Solution Using a Static and Homogeneous Field of 10 T. *Japanese Journal of Applied Physics* **1999**, 38, 842-844.
45. Zhanyong, W., Hui, X. U., Jiansen, N., Qiang, L., & Bangxin, Z., Effect of High Magnetic Field on the Crystallization of Nd2Fe14B/α-Fe Nanocomposite magnets. *Rare Metals* **2006**, 25, 337-341.
46. Zhanyong, W. A. N. G., Wenqing, L. I. U., Bangxin, Z. H. O. U., Jiansen, N. I., Hui, X. U., & Qiang, L. I. Microstructural Characteristics of Nd2Fe14B/α-Fe Nanocomposite Ribbons Bearing Nb Element. *Rare Metals* **2008**, 27, 299-302.
47. Zhuang, Y. X.; Chen, J.; Liu, W. J.; He, J.C. Effect of High Magnetic Field on Crystallization of Zr46.75Ti8.25Cu7.5Ni10Be27.5 Bulk Metallic Glass. *Journal of Alloys and Compounds* **2010**, 504S, 256-259.
48. Madsen, H. E. L.; Theory of Electrolyte Crystallization in Magnetic Field. *Journal of Crystal Growth* **2007**, 305, 271-277.
49. Coey, J.M.D.; Magnetic Water Treatment–How Might it Work?. *Philosophical Magazine* **2012**, 92, 3857-3865.
50. Powell, M. R.; Magnetic Water and Fuel Treatment: Myth, Magic, or Mainstream Science?. *Skeptical Inquirer* **1998**, 22.1, 27-31.
51. Swann, S.; Magnetron Sputtering. *Physics in Technology* **1988**, 19, 67-75.
52. Matsuda, T.; Umeda, K.; Kato, Y.; Nishimoto, D.; Furuta, M.; Kimura, M. Rare-metal-free high-performance Ga-Sn-O thin film transistor *Scientific Reports* **2017**, 7, 44326-44332. DOI: 10.1038/srep44326
53. Sudha, C.; Sivanarendiran, R.; Srinivasan, K. Influence of Magnetic Field on the Nucleation Rate Control of Mono Paracetamol. *Crystal Research and Technology* **2015**, 50, 230-235. DOI 10.1002/crat.201400432
54. Chibowski, E.; Szcześ, A., Magnetic Water Treatment–a Review of the Latest Approaches. *Chemosphere* **2018**, doi: 10.1016/j.chemosphere.2018.03.160.