Dynamic Aurora PLD with Si and porous Si to prepare ZnFe$_2$O$_4$
Thin films for liquefied petroleum gas sensing

Hiroki ISHIGAMI$^1$, Takahiko KAWAGUCHI$^1$, Naonori SAKAMOTO$^{1,2}$, Shenglei CHE$^{2,3,4}$, Nobuyoshi KOSHIDA$^5$, Kazuo SHINOZAKI$^{2,6}$, Hisao SUZUKI$^{1,2,7}$ and Naoki WAKIYA$^{1,2,7}$

1 Graduate School of Integrated Science and Technology, Department of Engineering, Shizuoka University, 3–5–1 Johoku, Naka-ku, Hamamatsu 432–8561, Japan
2 Research Institute of Electronics, Shizuoka University, 3–5–1 Johoku, Naka-ku, Hamamatsu 432–8561, Japan
3 College of Materials Science and Engineering, Zhejiang University of Technology, Hangzhou 310014, China
4 Research Center of Magnetic and Electronic Materials, Zhejiang University of Technology, Hangzhou 310014, China
5 Graduate School of Engineering, Tokyo University of Agriculture and Technology, 2–24–16 Naka-cho, Koganei, Tokyo 184–8588, Japan
6 School of Materials and Chemical Technology, Tokyo Institute of Technology, 2–12–1 O-okayama, Meguro-ku, Tokyo 152–8550, Japan
7 Graduate School of Science and Technology, Shizuoka University, 3–5–1 Johoku, Naka-ku, Hamamatsu 432–8561, Japan

Polycrystalline ZnFe$_2$O$_4$ thin films were deposited on Si and porous Si (PSi) substrates using Dynamic Aurora pulsed laser deposition (PLD in a magnetic field). The average grain sizes of ZnFe$_2$O$_4$/Si and ZnFe$_2$O$_4$/PSi were, respectively, 120 and 48 nm. The ZnFe$_2$O$_4$/PSi thin film resistance was higher than that of ZnFe$_2$O$_4$/Si thin film. For ZnFe$_2$O$_4$/Si and ZnFe$_2$O$_4$/PSi thin films, the sensor response for liquefied petroleum gas was measured as a function of time and temperature. The sensor response of ZnFe$_2$O$_4$/PSi thin film measured at 375 °C is higher than that of ZnFe$_2$O$_4$/Si thin film. Results showed a steep initial rise in the temperature dependence of ZnFe$_2$O$_4$ thin films prepared using PLD. The dependence is steeper than that reported for ZnFe$_2$O$_4$ powder or thick and thin films prepared using chemical processing.

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1. Introduction

Semiconductor gas sensors have been investigated intensively to detect reducing gases such as liquefied petroleum gas (LPG), carbon monoxide (CO), methane (CH$_4$), ethanol (C$_2$H$_5$OH), hydrogen sulfide (H$_2$S), hydrogen (H$_2$), and chlorine (Cl$_2$). The semiconductor gas sensor made of metal oxide was first reported by Seiyama et al.\textsuperscript{1)} Since then, metal oxides such as ZnO, In$_2$O$_3$ and especially SnO$_2$ have been investigated as semiconductor gas sensors.\textsuperscript{2,3)} However, an important difficulty associated with these materials is low selectivity: distinguishing one target reducing gas from other interfering reducing gases is difficult. Spinel ferrites with general formula ABO$_4$ are promising for use as gas sensor materials because they show more selectivity than the metal oxides described above.\textsuperscript{4,5)} The reason for greater selectivity in spinel ferrites is ascribed to the fact that the spinel structure comprises two cation sites (A and B sites), which brings about different chemical characteristics and charge states. The first report of gas sensor response properties on spinel ferrite described results obtained for ZnFe$_2$O$_4$.\textsuperscript{6)} Since then, gas sensor response has been reported for many spinel ferrites such as NiFe$_2$O$_4$, CuFe$_2$O$_4$, CdFe$_2$O$_4$, CoFe$_2$O$_4$, and MgFe$_2$O$_4$.\textsuperscript{7)}

Gas sensors have been fabricated as pellets, thick films, and thin films. Using them, sensor responses for reducing gases are measured. For ZnFe$_2$O$_4$, prepared reportation processes are described briefly below. Pellet-form gas sensors have been fabricated by sintering nano-sized ZnFe$_2$O$_4$ powder synthesized using sol–gel auto-combustion method.\textsuperscript{8)} Thick-film-form gas sensors have been fabricated by coating a paste made of nano-sized ZnFe$_2$O$_4$ powder and organics such as polyvinyl alcohol (PVA) on planar or tubular substrates. Nano-sized ZnFe$_2$O$_4$ powders have been synthesized using sol–gel method,\textsuperscript{9,10)} co-precipitation method,\textsuperscript{11,12)} hydrothermal method,\textsuperscript{13)} sol–gel auto-combustion method,\textsuperscript{14)} and molten-salt method.\textsuperscript{15)} Thick-film-form gas sensors have also been fabricated using suspension plasma-sprayed method,\textsuperscript{16,17)} Thin-film-form gas sensors have been fabricated using spin coating\textsuperscript{18,19)} and spray pyrolysis\textsuperscript{18,19)} of sol–gel-derived ZnFe$_2$O$_4$ precursor.
solutions on alumina or Si substrates. The microstructures of these gas sensors fabricated using nano-sized ZnFe$_2$O$_4$ powder and sol–gel derived ZnFe$_2$O$_4$ precursor solutions is porous \cite{10,12,13,14,15,16,17} or has nanorods \cite{18,19} to increase the surface area and thereby enhance sensor response. Using a porous alumina template, Zhang et al. prepared ZnFe$_2$O$_4$ nanotubes having approximately 200 nm outer diameter with a 20-nm-thick wall. \cite{20,21} They immersed commercial anodic aluminum oxide membranes into the PVA-assisted Zn/Fe nitrate precursor to impregnate the precursor in the membrane channel. Then the membrane was dried and calcined in a furnace. They repeated this “drip-dry-calcination” process three times. Finally, they immersed the membrane in NaOH solution to dissolve the template and thereby obtain ZnFe$_2$O$_4$ nanotubes.

As described above, all reported ZnFe$_2$O$_4$ gas sensors were fabricated using nano-sized ZnFe$_2$O$_4$ powder or sol–gel derived ZnFe$_2$O$_4$ precursors. No report to date has described the fabrication of ZnFe$_2$O$_4$ thin film gas sensors using physical vapor deposition (PVD) such as sputtering and pulsed laser deposition (PLD). This situation is the same for all other ferrite gas sensors such as NiFe$_2$O$_4$, CuFe$_2$O$_4$, CdFe$_2$O$_4$, CoFe$_2$O$_4$, and MgFe$_2$O$_4$. Although many reports have described the use of PVD to prepare ferrite thin films for magnetic and high-frequency applications, no report of the relevant literature has described a study of gas sensors. This might be true because PVD-derived thin films generally have a very flat and smooth microstructure associated with a low surface area.

The semiconductor gas sensor principle is the change of electric resistance by adsorption and desorption of oxygen. When oxygen in air is adsorbed onto the ZnFe$_2$O$_4$ surface, the adsorbed oxygen extracts electrons from the bulk to ionize into $O^-$ or $O^{2-}$. This extraction leads to formation of a thin electron depleted layer that increases the height of the potential barrier between ZnFe$_2$O$_4$ grains to increase electric resistance because ZnFe$_2$O$_4$ is an n-type semiconductor. When a reducing gas is introduced, interaction of the reducing gas with surface-adsorbed oxygen takes place, which brings about a release of electrons to decrease the height of the potential barrier between ZnFe$_2$O$_4$ grains and thereby decrease resistance. \cite{22} This mechanism is expected to be applicable for PVD-derived thin films deposited on a flat substrate such as Si. Additionally, it is expected that the sensor response of gas sensor will be increased for PVD thin film deposition on a substrate having high surface area such as porous Si (PSi). This work was conducted to prepare ZnFe$_2$O$_4$ thin films using Dynamic Aurora PLD \cite{23,24,25} on Si and PSi substrates, and to compare their LPG sensing properties with other materials described in the literature to evaluate the PVD-derived thin film performance.

## 2. Experimental

Using Dynamic Aurora PLD with a Nd:YAG laser ($\lambda = 266$ nm), ZnFe$_2$O$_4$ thin films were deposited on Si and PSi substrates. For this PLD, an electromagnet was installed in the vacuum chamber between a target and a substrate. Therefore, a magnetic field parallel to the direction from the target to the substrate is applicable during thin film deposition. Our earlier work revealed that application of a magnetic field during deposition brings about convergence of the PLD plume (plasma) to increase the deposition rate. \cite{26,27} For the present study, thin film deposition was conducted under a 1,000 G magnetic field. Detailed deposition conditions are presented in Table 1. A ZnFe$_2$O$_4$ target with stoichiometric composition was synthesized using a conventional solid state reaction with ZnO (99.99%, Kojundo Chemical Lab. Co. Ltd., Japan) and $\gamma$-Fe$_2$O$_3$ (99%, Kojundo Chemical Lab. Co. Ltd., Japan). The powders were mixed using a mortar and a pestle, and were calcined at 800 °C for 2 h. The calcined powder was ground, pressed into a pellet, and sintered at 1,350 °C for 4 h to synthesize a ZnFe$_2$O$_4$ target.

For this study, PSi was prepared by electrochemical anodization of Sb-doped polished n-type Si(001) wafers with resistivity of 0.008–0.02 Ω cm. The wafers were placed into a laboratory-made Teflon holder and were connected to the anode of a potentiostat/galvanostat (HAL3001A with attached 10 A booster unit; Hokuto Denko Corp., Japan). A Pt wire was connected to the potentiostat/galvanostat cathode. The electrolyte contains 46–48% aqueous hydrogen fluoride (HF) and 99.5% ethanol with a volume mixing ratio of 1:1 (27.3 wt % of HF). Anodization was conducted using the galvanostat mode of 100 mA/cm$^2$ for 300 s.

The ZnFe$_2$O$_4$ thin films deposited on Si and PSi substrates were characterized using X-ray diffractometry (MRD; Malvern Panalytical, UK). Film compositions and thicknesses were measured using an X-ray fluorescence spectrometer (XRF) (Minipal; Malvern Panalytical, UK) equipped with the FP Multi software module. Surface microstructures and film cross-sections were observed using scanning electron microscopy (SEM, JSM-7001F; JEOL, Japan).

On the ZnFe$_2$O$_4$ thin film surface, 1.1 mm$\phi$ Pt electrodes were fabricated through a metal mask. Resistance of the film was measured using two-probe method. Gas sensing properties were measured using the laboratory-made apparatus presented in Fig. 1. In this work, the change of resistance with time and the change of sensor response (S) with temperature were measured. The sensor response (S) was defined as the following.

\[ S(\%) = \frac{|R_a - R_{g1}|}{R_a} \times 100 \]
Therein, $R_a$ and $R_g$ respectively represent resistance in air and in the reducing gas. The change of resistance with time was measured as described below. After setting the sample in the measurement chamber in air, the air was evacuated to $1.0 \times 10^4$ Pa. The resistance was measured at this pressure ($R_a$). Then the chamber was evacuated again to $1.0 \times 10^3$ Pa. At this pressure, pure LPG was introduced into the chamber to $1.0 \times 10^4$ Pa. Resistance measurement in the gas ($R_g$) was started immediately after introducing pure LPG into the chamber. The measurement procedure in this work is presented schematically in Fig. 2.

3. Results and discussion

Figures 3(a) and 3(b) show SEM images of the surface and cross-section of PSi substrate prepared using anodic oxidation. Figure 3(c) portrays an enlarged image of the cross-section at the Si–PSi interface. These figures show that the PSi substrate comprises vertical straight pores having average pore diameter of 13.4 nm and pore length of 46 μm. The fraction of the surface pore analyzed using ImageJ software\(^{27}\) was 15%. On Si and PSi substrate, ZnFe$_2$O$_4$ thin films were deposited. Measurement by XRF revealed that the composition of thin film deposited on Si and PSi are, respectively, Zn$_{0.41}$Fe$_{2.59}$O$_4$ and Zn$_{0.38}$Fe$_{2.62}$O$_4$. Therefore, the ZnFe$_2$O$_4$ thin films have Fe-rich composition. Figure 4 shows XRD patterns of ZnFe$_2$O$_4$ thin film deposited respectively on (a) Si and (b) PSi substrates. The ZnFe$_2$O$_4$/Si thin film is polycrystalline having (111) preferential orientation. ZnFe$_2$O$_4$/PSi thin film is polycrystalline without (111) preferential orientation. The difference
of orientation is apparent from the fact that the PSi substrate surface is rougher than that of the Si substrate. Figures 5(a) and 5(b) respectively portray SEM images of the surface and cross-section of ZnFe$_2$O$_4$/Si thin film. Figures 5(c) and 5(d) respectively portray SEM images of the surfaces and cross-sections of ZnFe$_2$O$_4$/PSi thin films. Figures 5(b) and 5(d) show that the thickness of ZnFe$_2$O$_4$ thin film deposited on Si and PSi substrates is equal to 190 nm, as confirmed also by XRF. These figures indicate that the ZnFe$_2$O$_4$ thin films deposited on Si and PSi are dense. Figures 5(a) and 5(c) show that the grain size of ZnFe$_2$O$_4$ thin film deposited on Si is much greater than that deposited on PSi. From analysis using ImageJ software, the average grain sizes of ZnFe$_2$O$_4$ thin film deposited on Si and PSi are, respectively, 120 and 48 nm. The small grain size of ZnFe$_2$O$_4$ thin film deposited on PSi indicates that the density of nucleation sites on the surface of PSi is much higher than that of the Si substrate, as depicted schematically in Fig. 6.

Figure 7 shows the change of resistance of (a) ZnFe$_2$O$_4$/Si and (b) ZnFe$_2$O$_4$/PSi thin films with time after introducing LPG in the measurement chamber at 375 ºC. The $R_s$ values of ZnFe$_2$O$_4$/Si and ZnFe$_2$O$_4$/PSi thin films were, respectively, 93.2 and 4230 kΩ. After introducing LPG, the resistivity of both samples decreased, which proves that ZnFe$_2$O$_4$ thin film is an n-type semiconductor.$^{6,7}$ Figure 7 depicts that the ZnFe$_2$O$_4$/PSi thin film resistance is at least one order higher than that of ZnFe$_2$O$_4$/Si thin film during measurement. Figure 5 shows that the ZnFe$_2$O$_4$/PSi grain size is smaller than that of ZnFe$_2$O$_4$/Si thin film. Therefore, the grain boundary density is responsible for the potential barrier being higher for ZnFe$_2$O$_4$/PSi to have increased resistance. Figure 8 shows the change of sensor response of (a) ZnFe$_2$O$_4$/Si and (b) ZnFe$_2$O$_4$/PSi thin films over time after introducing LPG measured at 375 ºC. This figure indicates that ZnFe$_2$O$_4$/PSi thin film has a steeper initial rise and higher sensor response than ZnFe$_2$O$_4$/Si thin film. Therefore, ZnFe$_2$O$_4$ thin film deposited on the PSi substrate is promising for use as a gas sensor.

Mukherjee and Majumder$^{28}$ reported that the change of conductance with time $G(t)$ is given as the following based
Langmuir adsorption kinetics for a single adsorption site under the assumption that the conductance is proportional to the concentration of the reducing gas and monolayer coverage of reducing gas as

\[ G(t) = G_0 + G_1 \left[ 1 - \exp\left( -\frac{t}{\tau} \right) \right] \]  

where \( G_0 \) represents the conductance at \( t \) of zero, \( G_1 \) is a coefficient, and \( \tau \) denotes the relaxation time. It is noteworthy that \( G(\infty) = G_0 + G_1 \), where \( G(\infty) \), the conductance at \( t \) is sufficiently large.

This equation can be converted to the following equation.

\[ \ln[G(\infty) - G(t)] = -\frac{t}{\tau} + \ln G_1 \]  

In that equation, \( G \) is the inverse of the resistance. Therefore, the data portrayed in Fig. 7 can be replotted as Fig. 9. In Fig. 9, the change of \( \ln[G(\infty) - G(t)] \) with time is shown until \( t = 500 \) s to elucidate the mechanism of the initial stage. Figure 9 depicts that the slope of the line changes at around 90 s for both ZnFe\(_2\)O\(_4\)/Si and ZnFe\(_2\)O\(_4\)/PSi thin films. Figure 9(c) depicts the change of temperature of ZnFe\(_2\)O\(_4\)/Si thin film with time. As described in the experimental part, the measurement of \( R_g \) was started immediately after introducing LPG in the chamber. By introducing LPG in the chamber, the sample temperature increases by adiabatic compression. Figure 9(c) shows that the temperature change finished within 20 s. The sample temperature was constant within fluctuation of the temperature controller (±0.2 °C). A similar tendency was observed for the ZnFe\(_2\)O\(_4\)/PSi thin film. This result suggests that the change of chamber pressure is negligible after 20 s. Therefore, changes of slope at 90 s shown in Figs. 9(a) and 9(b) are not attributable to the change of temperature and pressure during measurements. As presented respectively in Figs. 9(a) and 9(b), the respective relaxation times \( \tau \) before and after 90 s for ZnFe\(_2\)O\(_4\)/Si are 530 and 760 s; those for ZnFe\(_2\)O\(_4\)/PSi are 110 and 180 s. The fact that two
The sensor response of ZnFe$_2$O$_4$ became almost negligible.

Goutham et al.\textsuperscript{14} reported that ZnFe$_2$O$_4$ powder synthesized using sol–gel auto combustion method shows a maximum sensor response of 80\% at 375°C. This peak temperature is almost equal to that found for the ZnFe$_2$O$_4$/PSi thin film. Goutham et al.\textsuperscript{14} reported that ZnFe$_2$O$_4$ powder synthesized using sol–gel auto combustion method shows a maximum sensor response of 80\% at 375°C. This peak temperature is almost equal to that found for the ZnFe$_2$O$_4$/PSi thin film.

Fig. 10 shows that the temperature dependence of the sensor response and the maximum sensor response temperature depends on the method used for sample preparation. As described in the Introduction, this is the first report of work to measure the sensor response of reducing gases by thin films prepared using PLD on Si and PSi substrates. The results presented in Fig. 10 suggest that PLD-prepared ZnFe$_2$O$_4$ thin film deposited on PSi shows a high maximum sensor response, although the temperature of the maximum sensor response is rather high. This figure also shows that the temperature-dependence of ZnFe$_2$O$_4$ thin film prepared using PLD shows a steep initial rise. The reason for the steep initial rise remains unclear. A possible reason for the steep rise is related to the fact that PLD-derived thin films have a smaller surface area than thick films composed of sol–gel-derived or co-precipitation-derived powders. This result suggests that charge transfer at the thin film surface would occur more quickly than that of powders. In general, a steep initial rise will help to distinguish a target-reducing gas from other interfering reducing gases. Therefore, it is expected that the ZnFe$_2$O$_4$/PSi thin film will show high selectivity. To confirm this point, measurement of the temperature dependence of the sensor response for other gases such as CO is under study.

4. Conclusions

A representative gas-sensing material, ZnFe$_2$O$_4$, is used for semiconductor gas sensors of reducing gases. To date, gas sensors have been fabricated using chemical processing such as sol–gel-derived or co-precipitation-derived ZnFe$_2$O$_4$ powders, and thick and thin films. However, no report describes fabrication of gas sensors using PVD. This report is the first of work conducted to prepare ZnFe$_2$O$_4$ thin films using PLD (Dynamic Aurora PLD) for application to gas sensors. The average grain sizes of ZnFe$_2$O$_4$/Si and ZnFe$_2$O$_4$/PSi were, respectively, 120 and 48 nm. The resistance of ZnFe$_2$O$_4$/PSi thin film was higher than that of ZnFe$_2$O$_4$/Si thin film. For ZnFe$_2$O$_4$/Si and ZnFe$_2$O$_4$/PSi thin films, the sensor response for LPG was measured as a function of time and temperature. The sensor response measured at 375°C of ZnFe$_2$O$_4$/PSi thin film is higher than that of ZnFe$_2$O$_4$/Si thin film. Results show that the temperature dependence of ZnFe$_2$O$_4$ thin films prepared using PLD shows a steep initial rise. That rise is steeper.
than the rise for reported ZnFe$_2$O$_4$ powder and thick and thin films prepared using chemical processing.

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**References**

1) T. Seiyama, A. Kato, K. Fujiishi and M. Nagatani, *Anal. Chem.*, 34, 1502–1503 (1962).
2) J. F. Boyle and K. A. Jones, *J. Electron. Mater.*, 6, 717–733 (1977).
3) G. Korotcenkov, *Mater. Sci. Eng. B-Adv.*, 139, 1–23 (2007).
4) S. Darshane and I. S. Mulla, *Mater. Chem. Phys.*, 119, 319–323 (2010).
5) A. Sutka and K. A. Gross, *Sensor. Actuat. B-Chem.*, 222, 95–105 (2016).
6) C. Xiangfeng, L. Xingqin and M. Guangyao, *Sensor. Actuat. B-Chem.*, 55, 19–22 (1999).
7) A. B. Gadkari, T. J. Shinde and P. N. Vasambekar, *IEEE Sens. J.*, 11, 849–861 (2011).
8) A. Sutka, G. Mezinskis, A. Lusis and D. Jakovlevs, *Sensor. Actuat. B-Chem.*, 171–172, 204–209 (2012).
9) S. Singh, A. Singh, R. R. Yadav and P. Tandon, *Mater. Lett.*, 131, 31–34 (2014).
10) E. R. Kumar, P. S. P. Reddy, G. S. Devi and S. Sathiyaraj, *J. Magn. Magn. Mater.*, 398, 281–288 (2016).
11) N. S. Chen, X. J. Yang, E. S. Liu and J. L. Huang, *Sensor. Actuat. B-Chem.*, 66, 178–180 (2000).
12) A. F. S. Abu-Hani, S. T. Mahmoud, F. Awwad and A. I. Ayesh, *Sensor. Actuat. B-Chem.*, 241, 1179–1187 (2017).

13) X. Chu, D. Jiang and C. Zheng, *Mater. Sci. Eng. B-Adv.*, 129, 150–153 (2006).
14) S. Goutham, D. S. Kumar, K. K. Sadasivuni, J. J. Cabibihan and K. V. Rao, *J. Electron. Mater.*, 46, 2334–2339 (2017).
15) S. L. Darshane, R. G. Deshmukh, S. S. Suryavanshi and I. S. Mulla, *J. Am. Ceram. Soc.*, 91, 2724–2726 (2008).
16) J. You, X. Chen, B. Zheng, X. Geng and C. Zhang, *J. Therm. Spray Techn.*, 26, 728–734 (2017).
17) A. Singh, A. Singh, S. Singh, P. Tandon, B. C. Yadav and R. R. Yadav, *J. Alloy. Compd.*, 618, 475–483 (2015).
18) Z. Jiao, M. Wu, J. Gu and Z. Qin, *IEEE Sens. J.*, 3, 435–438 (2003).
19) A. Sutka, J. Zavickis, G. Mezinskis, D. Jakovlevs and J. Barloti, *Sensor. Actuat. B-Chem.*, 176, 330–334 (2013).
20) G. Y. Zhang, B. Guo and J. Chen, *Sensor. Actuat. B-Chem.*, 114, 402–409 (2006).
21) G. Y. Zhang, C. Li, F. Cheng and J. Chen, *Sensor. Actuat. B-Chem.*, 120, 403–410 (2007).
22) M. Batzill and U. Diebold, *Prog. Surf. Sci.*, 79, 47–154 (2005).
23) N. Wakiya, N. Sakamoto, S. Koda, W. Kasasaka, N. Debnath, T. Kawaguchi, T. Kiguchi, K. Shinozaki and H. Suzuki, *NPG Asia Mater.*, 8, e279 (2016).
24) N. Wakiya, T. Kawaguchi, N. Sakamoto, H. Das, K. Shinozaki and H. Suzuki, *J. Ceram. Soc. Jpn.*, 125, 856–865 (2017).
25) N. Debnath, T. Kawaguchi, W. Kasasaka, H. Das, K. Shinozaki, N. Sakamoto, H. Suzuki and N. Wakiya, *J. Magn. Magn. Mater.*, 432, 391–395 (2017).
26) N. Debnath, T. Kawaguchi, H. Das, S. Suzuki, W. Kasasaka, N. Sakamoto, K. Shinozaki, H. Suzuki and N. Wakiya, *Sci. Technol. Adv. Mater.*, 19, 507–516 (2018).
27) C. A. Schneider, W. S. Rasband and K. W. Eliceiri, *Nat. Methods*, 9, 671–675 (2012).
28) K. Mukherjee and S. B. Majumder, *J. Appl. Phys.*, 106, 064912 (2009).
29) S. P. Dalawai, T. J. Shinde, A. B. Gadkari and P. N. Vasambekar, *J. Mater. Sci.-Mater. El.*, 26, 9016–9025 (2015).