EFECTUL CONȚINUTULUI ÎN Mn ASUPRA PROPRIETĂȚILOR MAGNETICE ŞI STRUCTURALE ALE GaN:Mn PE SUBSTRAT DE SILICIU PRIN METODA DEPUNERII DIN SOLUȚIE CHIMICĂ

EFFECT OF Mn CONCENTRATION ON MAGNETIC AND STRUCTURAL PROPERTIES OF GaN:Mn DEPOSITED ON SILICON SUBSTRATE USING CHEMICAL SOLUTION DEPOSITION METHOD

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The objective of this research was to study the change of Mn mole fraction to the structure and magnetic properties of GaN:Mn thin film by sol-gel method. A thin film ferromagnetic semiconductor of GaN:Mn has been deposited on Si(111) substrate by using Chemical Solution Deposition method (CSD) and spin coating technique. Atomic composition, crystal structure, morphology and magnetic properties of the GaN:Mn thin film were characterized using Energy dispersive of X-ray (EDX), X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Scanning Probe Microscopy (SPM) and Vibrating Sample Magnetometer (VSM). The results showed that the GaN:Mn thin film still contains carbon atom impurity and non-stochiometri. The GaN:Mn thin film has polycrystalline form in which the 2θ angle of GaN peaks have been shifted (~ 0.22^o) for that with Mn composition of 5.24% at 32.62° angle. SEM and SPM investigation show the surface of GaN:Mn thin film with 6% Mn distributed by homogeneous grains and the level of surface roughness was 15.3 to 29.90 nm. However, the other magnetic phases ($Ga_{5-2}Mn$) and oxide phases of Mn, Si and Ga were also detected in the GaN:Mn thin films. Sample with 7.43% Mn exhibits optimum composition results in appearance of ferromagnetic properties. The remanent magnetic (M_r) and saturation magnetic (M_s) of sample were achieved at 5.04 emu/cm^3 and 91.5 emu/cm^3, respectively.

Keywords: *GaN:Mn; Chemical Solution Deposition; spin coating; Si(111) substrate; magnetic properties; ferromagnetic*

1. Introduction

Recent growth of computation and communication technologies needs support of high precision electronic devices. Development of spintronic-based electronic devices is a real step forward to new information and communication technologies. Spintronic devices have many applications, such as for sensor, magnetic random access memory, quantum computing, data storage, and switching. The devices have an advantage of their compactness as compared to a conventional semiconductor. The devices have also lower working voltage which consequently reduces their energy requirement. Thus, a material that is suitable for spintronic devices preparation must have electronic properties (semiconductor) and magnetic spin (ferromagnetic) [1,2].

Dilute Magnetic Semiconductor (DMS) material is appropriate material for application of spintronic devices due to the spin of magnetic materials as electron energy. Magnetic atom in DMS is mainly filled by transition metals of *d* orbital (Sc, Ti, V, Cr, Mn, Fe, Co, Ni, and Cu) and *f* orbital (Eu, Gd, Er). Atoms in d and f orbitals are atoms whose unpaired electrons which depend on their spin and show magnetic properties of the material [3-5]. However, most of the DMS materials exhibits ferromagnetic properties slightly above room temperature where at room temperature, the DMS does not require cooler or heater to maintain the properties. Therefore the DMS material with ferromagnetic properties at room temperature is required. In theory, gallium nitride (GaN) material doped with manganese (Mn) will become DMS material that can be used at room temperature [6]. This phenomenon is supported by many previous research findings. They reported that the properties of ferromagnetism in semiconductor arose at above room temperature, which was formed by materials of group III-V and II-VI including transition-metal-doped ZnO, GaN, and dilute magnetic oxide (DMO) [4]. Shinichi (2008) reported that GaN doped by 9% Mn atomic through deposition of MBE (Molecular Beam epitaxy) has a Curie temperature of 940 K [7]. Takano et al (2006) reported that through MBE method, the structural and magnetic properties of the GaN:Mn at high Mn composition (>5%) were observed to be governed by precipitate clusters of anti-ferromagnetic $GaMn_3N$ and ferromagnetic Mn_4N [8]. However, study on GaN:Mn by using chemical solution deposition (CSD) is still limited in the literatures. Obradors et al (2003) stated that

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Chemical solution deposition (CSD) is a low cost alternative for the fabrication of conductors [9]. The main advantage of CSD besides of its lower cost, it also has low capital investment and it envisages supply costs. Moreover, the CSD becomes a competitive alternative to vapour deposition techniques which requiring the use of vacuum systems. The achievement of oxide epitaxial films using CSD was demonstrated more recently and it was shown that the growth of epitaxial layers has as driving force the elimination of grain boundaries in the random nanocrystalline film resulting after the pyrolysis [10].

This article was aimed to study thin layer of GaN:Mn ferromagnetic semiconductor deposited on silicon substrate (111) by using Chemical Solution Deposition and Spin Coating methods. In this study, the mole change of Mn during the deposition in the GaN:Mn thin film was observed particularly their effect on magnetic properties of the thin layer.

2. Materials and Methods

2.1. Materials and Thin Layer Preparation

The synthesis of crystal powder of manganese-gallium-citrate-amine was conducted through gel preparation. The gel was prepared from solutions of $Ga^{3+}$and Mn^{4+} ions and citric acid (CA) with the mole fraction of Mn/Ga 2-8 %. Ga_2O_3 powder and MnO_2 powders with a mole fraction of Mn/Ga 2-8 % the was dissolved in a mixture of 5 ml HCl and 5 ml HNO_3. The pH solution was adjusted 7.6 to 8 by adding ammonia hydroxide (NH_4OH) solution about 9 ml to obtain Ga^{3+} and Mn^{4+} ions. Citric acid was added to the solution such that the molar ratio of Ga:CA became 1:1.

The solution was stirred by using a magnetic stirrer at a temperature of 80 ^oC for 2 hours. The crystal was then filtered using filter paper, rinsed with acetone, and dried in a vacuum desiccator. The crystals were dissolved in 0.6 M ethylendiamine to form manganese-gallium citrate-amine gel and then were coated on a Si (111) substrate. Decomposition of nitrogen atoms was done by flowing nitrogen gas at a temperature of 900 ^oC such that the nitrogen atom became reactive and bind to the Ga atoms to form GaN layer.

2.2. Deposition Method

The deposition of a thin layer of GaN:Mn on Si (111) substrate was carried out by using spin coating technique.The deposition process was done by using gel of manganese-gallium-citrate amine by dissolving crystalline manganese-gallium-amine in 0.6 M citrate ethylendiamine.

Before the deposition process, the Si substrate was cleaned following Radio Corporation of America (RCA) methods.

The Si substrate was washed by acetone for 10 minutes and subsequently by methanol for 10 minutes under ultrasonic washing system to remove organic impurities i.e. fats and oils. Furthermore, the Si substrate was washed with deionized water (DI) for 1 minute and was soaked in 20% HF solution for 10 seconds to remove the SiO_2 layer formed during storage. After that, the substrate was washed with deionized water and then dried by spraying nitrogen (N_2) gas.

The dried Si (111) substrate was heated in a hot plate at temperature of 150 ^oC for 10 minutes. The substrate was then placed on a spin coater and dropped with a manganese-gallium citrate-amine gel. The substrate was rotated on the spin coater with a speed of 1200 rpm for 20 seconds. Furthermore, the sample was dried at a temperature of 150 ^oC for 10 minutes and subsequently was heated in a furnace at temperature of 350 ^oC for 20 minutes to remove the organic components in the layers. The sample was annealed at temperature 900 ^oC for 2 hour and in the same time the nitridation was carried out by flowing nitrogen with a flow rate of 4 sccm into the furnace. The increase of temperature of the furnace was set at 10 ^oC/minute. The nitrogen flow was implemented to provide a source of N precursor in order to form Ga^{3+} and N^{3+} anions bonding which later turn as GaN:Mn layer.

Doping of manganese was applied such that a magnetic moments of electrons of Mn atom may be generated on the thin GaN layer. Effect of Mn composition on the thin layer of semiconductor was characterized by using Energy Dispersive X-ray spectroscopy (EDX) and Scanning Electron Microscopy (SEM) series JEOL JSM-6360LA, X-ray Diffraction (XRD) type Phillips PW 1710 with operating conditions: Cu Kα1=1.54056 Å, and Squid Vibrating Sample Magnetometer (VSM). The XRD data was confirmed with Join Committee on Powder Diffraction Standard (JCPDS). The database (PDF number fro XRD) of each component are Ga_2O_3 with PDF#431013, MnO_2 with PDF#390375, GaN with PDF#021078, $Ga_{5.2}Mn$ with PDF#240437, Si with PDF#271402, SiO_2 with PDF#450131, Mn_2O_3 with PDF#411442 and Mn_3O_4 with PDF#240734.

3. Results and Discussion

Table 1 depicts EDX characterization of the thin GaN:Mn layer resulted from peaks of EDX spectra. The EDX spectra merely includes Ga, Mn, Si, N, and C atoms. The C atomic spectrum on the thin layer may due to incomplete gel preparation. This C atoms probably came out during gel preparation in which citrate amine ($C_6H_8O_7.H_2O$) and ethylenediamine ($C_2H_8N_2$) precursors were used. This research also showed that the Ga/N

Table 1

Atomic composition of EDX characterization of the GaN:Mn thin film at various Mn/Ga mole fraction

Mn/Ga mole fraction (solution)	EDX Composition (%)					Ga/N Ratio	Mn incorporated in GaN (%)
	Mn	Ga	N	C	Si		
0.02	0.05	3.38	2.26	9.63	84.6	1.49	1.45
0.04	0.36	4.48	1.10	7.33	86.7	4.07	7.43
0.06	1.08	8.26	6.23	30.0	54.3	1.30	11.60
0.08	0.65	11.8	5.46	19.1	63.0	2.15	5.24

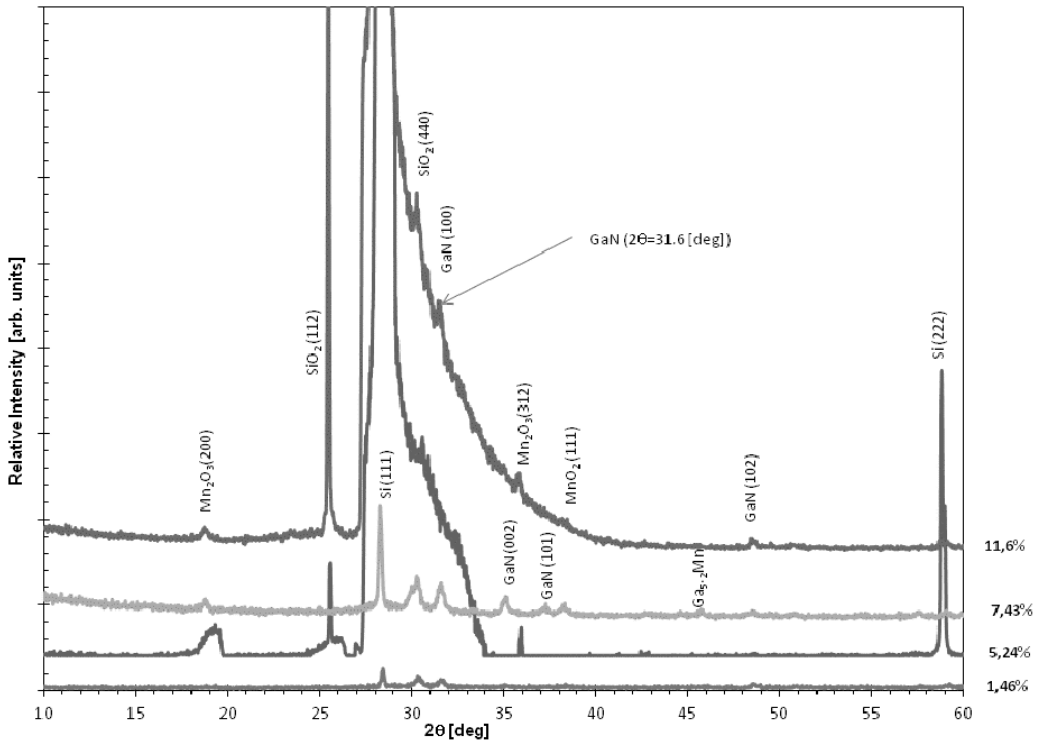

Fig. 1 - XRD patern of the thin GaN:Mn layer samples with Mn composition of 1.46%, 5.24%, 7.43%, and 11.6%. The GaN(100) was detected at 2θ=31.6 [deg] and it was lower than the reference PDF#021078 (2θ=32.4 [deg]).

atomic ratio was greater than 1 which may due to nitrogen vacancy available in the thin layer. This phenomenon proved that the GaN thin layer obtained from the experiment was n-type semiconductor. The n-type semiconductor is very suitable for ferromagnetism stabilization. In other hand, Ga atomic vacancies cause the GaN thin layer is a p-type semiconductor [11].

However, there were still atomic carbon impurities in the thin layer of GaN:Mn. Stoichiometric composition of the layer indicated that the thin layer is an n-type semiconductor due to presence of nitrogen vacancies. This phenomenon may cause the doped Mn atoms on the thin layer were difficult to attach in GaN layer. Consequently, the Mn atom tends to form a second phase or an oxide phase outside the GaN layer which eventually give anti-ferromagnetic properties. In addition, the nitrogen vacancies may change Ga atom to other phases of Mn or oxides.

All results of GaN:Mn thin layers showed that these layers were polycrystalline as depicted by XRD patern in Figure 1. Some peaks are assigned to GaN crystal, although some other peaks are also detected as Mn_2O_3, $Ga_{5.2}Mn$, MnO_2, and SiO_2. In overall, the GaN peaks are shifted by 2θ angle. The all 2θ angles of these peaks are shifted to second magnetic phase of GaMn as well as Mn oxides. In overall, the shifted angles of GaN peaks tends to move to a second magnetic phase angle peak GaMn and Mn oxide. This angle shift may be caused by the expansion of the crystal lattice in GaN due to the incorporation of Mn ions (Pradhan et al, 2012). The smallest angle shifting was showed by GaN:Mn with 5.24% Mn composition at 2θ angle of 32.62^o (based on PDF#021078) shifted by 0.22^o (Figure 1). Other appearance peaks were dominated by Mn and SiO_2 oxides such as MnO_2, Mn_2O_3, Mn_3O_4, SiO_2. In this layer, other phases of Ga were appeared such as are also exhibited such as Ga_2O_3 and $Ga_{5.2}Mn$.

The scanning electron microscopy (SEM) images and 3D images from Scanning Probe Microscopy (SPM) of GaN:Mn thin layers deposited on the Si (111) substrate with different

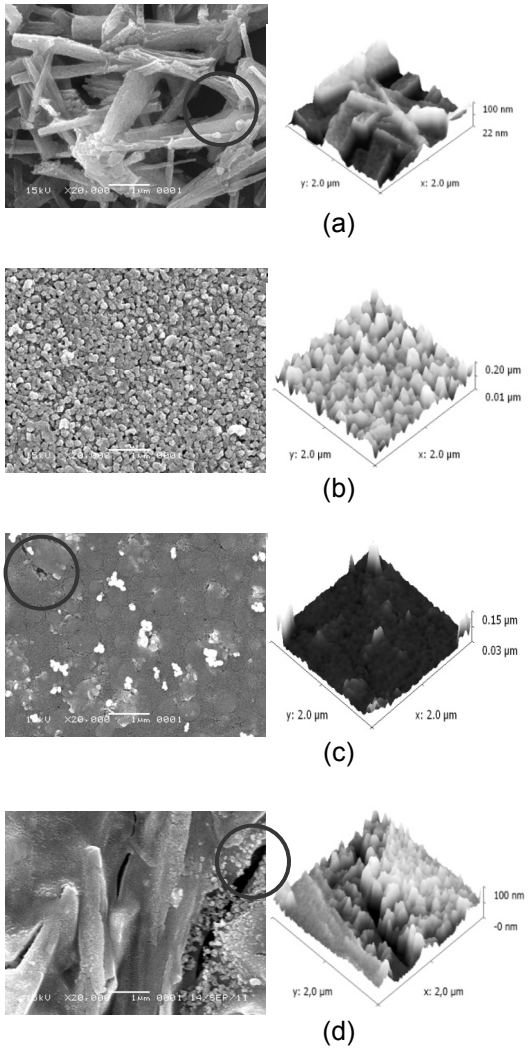

Fig. 2 - SEM surface morphology images and 3D morphology images of the thin layers of GaN:Mn with different mole fraction of Mn/Ga: (a) 4%, (b) 6%, (c) 8%, and (d) 10%.

mole fraction of Mn/Ga are shown in Figure 2. Figures 2 (a), (c), and (d) show that a thin layer of GaN:Mn with mole fraction of Mn/Ga 2%, 4%, 6%, and 8% have low uniformity in grain surface. The 2% Mn/Ga mole fraction exhibits a substrate surface which was not covered by the thin layer. The layer also shows that the thin layer were incompletely grow showing by set of rod-shaped granular form (red circle). The sample with 6% mole fraction shows agglomeration phenomena on the surface, while the 8% mole fraction shows cracking and islands-like formation on the surface layer. The thin layer with 4% mole fraction has the most homogeneous surface as compared to the other thin layers. The 2% mole fraction sample has the largest grain size of 197.4 nm, while the smallest grain sizes was achieved at 6% mole fraction of 167.9 nm.

Ferromagnetic semiconductor layer thickness of GaN: Mn deposition was recorded at 0.5 μm and it has a less homogeneous surface. This inhomogenity surface is probably due to the presence of impurities of carbon. The presence of impurities such as carbon in the substrate will decrease the acceleration of coalition process and the migration of grain boundaries occurs. If the impurities are present and covering a portion of the free surface of the crystal grains, then a thin surface layer with morphology composed of domes will be produced (Figure 3).

All samples of GaN:Mn thin layer showed hysteresis at room temperature. The samples with 5.24% Mn composition exhibits paramagnetic properties which higher than that of 1.46% Mn composition. Higher value of remanent magnetic becames an evidence that there was an influence of increasing Mn composition. The remanent magnetic shows a large number of magnetization that can be stored in the material when the magnetic field was removed [12]. The nitrogen vacancy(V_N) will remove and re-structure the electron states which may change its magnetic properties. Moreover, the nitrogen vacancy will give an effect of shallow donor. So the magnetic moment in the system involved one nitrogen vacancy is mainly attributed to the Ga atoms due to dangling bonds that created unpaired electrons, and the magnetic moments of Ga atom decrease rapidly as the distance of Ga atoms from V_N increases [3].

In addition, sample with 7.43% Mn composition showed ferromagnetic properties indicated by the emergence of magnetic saturation in the region of the hysteresis curve (Figure 4). Meanwhile, the samples with 11.6% Mn composition showed less sensitive magnetization to a given external field which may be due to influence of the contribution of antiferomagnetic at high Mn concentrations. The antiferromagnetic effect is most likely due to the Mn atoms that chemically bound to the sub-Ga. The Mn-Mn interactions that occur outside the substitution of Mn into Ga sub-lattice affects on the antiferromagnetic contributions. This suggestion refers to the emergence of Mn oxide phases such as Mn_2O_3 and MnO_2 from XRD characterization results of 11.6% Mn composition. The formed oxide phase was also more dominant than the other oxide phase samples such as Mn_2O_3(312) and MnO_2(111) with Mn composition of 11.6% and 7.43%, and $Ga_{5.2}Mn$ with Mn composition of 7.43%.

In overall, the magnetic properties of GaN:Mn thin layers has been changed from that of GaN itself. This led the Mn doping influences the magnetic properties of GaN and changes the state from diamagnetic to paramagnetic, ferromagnetic and antiferromagnetic [2]. Increasing Mn composition affects the changes in magnetic properties of the thin layer. However, the magnetic properties of the thin layer is not only originated from the substituted-Mn into the Ga matrix, but it was also influenced by the ferromagnetic properties of the second phase as

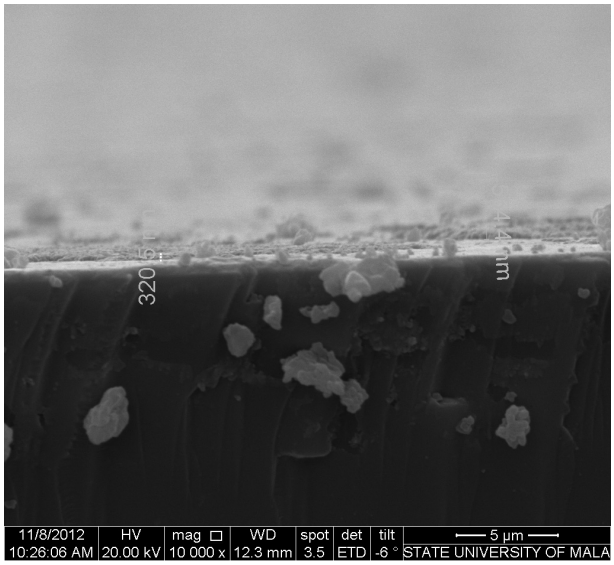

Fig. 3 - SEM surface morphology images show inhomogenity surface due to presence of carbon.

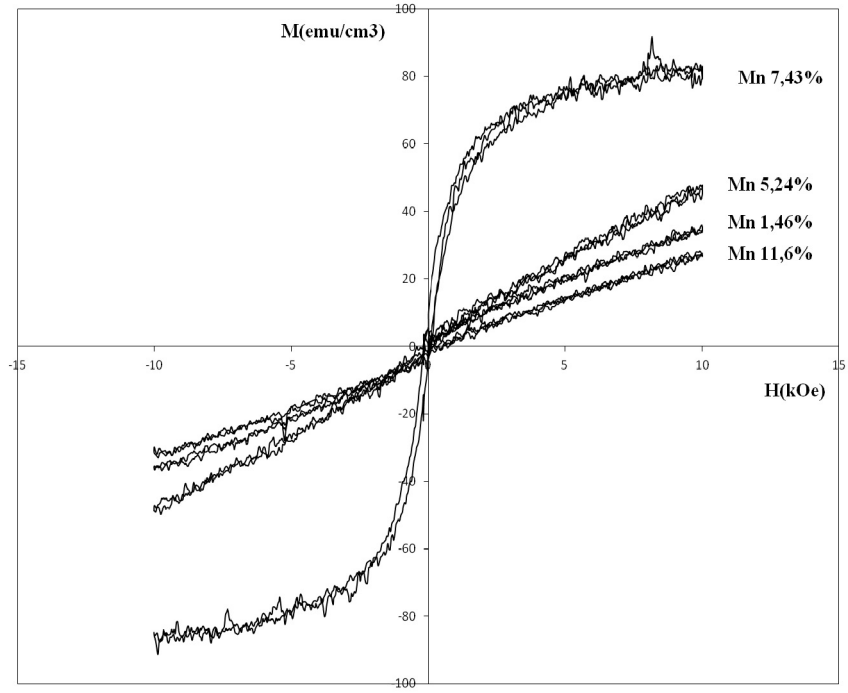

Fig. 4 - Hysteresis curve of M vs H from VSM characterization of the GaN:Mn thin layers with Mn composition of 1.46%; 5.24%; 7.44%; and 11.6%.

well as antiferomagnetic properties of Mn oxide. This phenomena is supported by the conclusions of Sato et al. [13]. The highest value of remanent magnetic (M_r) and saturation magnetic (M_s) of sample was 5.04 and 91.5 emu/cm^3, respectively for the sample with 7.43% Mn composition. The highest magnetic coercivity value of 157 Oe was found from 7.43% Mn composition sample, while the lowest one of 28.5 Oe was observed at the sample of 11.6% Mn composition. The optimum value of the magnetic properties of this study is on the sample with a composition of 7.43% Mn.

The deposition of ferromagnetic semiconductor layer GaN: Mn was also indicated by the presence of other phases such as $Ga_{5.2}Mn$, and SiO_2. This phase was present because of rapid dissociation and proceeding with removal of water and citrate-amine at high temperature (900 ^oC) to form a cluster of reactive nitrogen bonds. The other phase was determined during deposition such as MnO_2 and Mn_2O_3 which may because of lack of concentration GaN bonded to nitrogen [14]. This lack of concentration leads to difficulty in supporting Ga by Mn in GaN. In this case Mn tends to form other oxide compounds orh other magnetic phases. To reduce the occurrence of other phases than GaN: Mn, the deposition by using sol-gel deposition method can be done by changing the nitrogen gas (N_2) with ammonia gas (NH3) which is more reactive. In addition, the

sintering process should be done by flowing NH3 gas at a flow rate greater than 8 sccm at lower temperature of 700-750 ^{o}C. This lower temperature and high reactivity of N from NH3 dissociation, then the phase will be dominated bye GaN and GaN: Mn or in other words, the presence of other phase other than GaN: Mn can be reduced.

4. Conclusions

This study concluded that Chemical Solution Deposition (CSD) has been successfully applied for deposition of GaN:Mn thin film on Si substrate. The thin film of GaN:Mn still contains impurities of carbon atom and nitrogen vacancies. The thin film of GaN:Mn was polycrystalline structure which have shifted GaN peaks angles. The lowest shift showed by thin layer with a composition of Mn 5.24% at 2θ of 32.62° with a shift angle of ~ 0.22^{o}. In the layer, another magnetic phase of $Ga_{5.2}Mn$ and oxides of Mn, Si and Ga were still formed. Level of surface roughness of GaN:Mn thin layers was 15.3 to 29.90 nm. The size and homogeneous distribution of grains were formed in the thin layer with a mole fraction of Mn/Ga 6%. In the sample with 7.43% Mn composition shows optimum composition with the emergence of ferromagnetic properties with remanent magnetic (M_r), coercivity magnetic (M_c) and saturation magnetic (M_s) of 5.04 emu/cm^3, 157 Oe, and 91.5 emu/cm^3, respectively. Ferromagnetic properties of the thin layers of GaN:Mn was not only made through Mn-incorporated GaN phase, but also contributed by another magnetic phases and Mn oxide.

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