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Structural, Morphological and Acetone Sensing Properties of Ga doped ZnO Thin Films by Spray Pyrolysis

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***Abstract*:- The Ga doped ZnO thin films were deposited on preheated amorphous glass substrates using spray pyrolysis technique. The structural properties of Ga doped ZnO thin films produced by the spray pyrolysis method at 450 ^{0}C substrate temperature are studied. The films exhibit a dominant peak at 2θ = 34.44 corresponding to the (002) plane of ZnO. A uniform grain growth in all the film samples is observed from the SEM and TEM micrographs.**

Keywords: Spray pyrolysis; Ga-doped ZnO films; structural properties, SEM.

1. INTRODUCTION

Ga-doped ZnO (GZO) has drawn attentions recently because it has some advantages over AZO. Whereas AZO and GZO TCOs have comparable electrical properties [1], Ga dopant is less reactive with oxygen compared with Al dopant meaning that it can function as better dopant within ZnO [2]. In addition, the Ga- O covalent bond length of 1.92A˚ , which is smaller than that of Zn–O (1.97A˚), is expected to cause smaller deformation of ZnO lattice when Ga3+ ions substitute Zn2+ site in case of high doping concentration [3]. Concerning the use of Ga as the dopant to enhance electrical properties, it has been reported that resistivity of GZO films decreased with increasing film thickness where as the transmittance of films decreased as the film thickness increased [4]. On the practical side, increasing the thickness of the GZO TCO film would result in rising cost and reduced throughput. Further, as in the case of the AZO films, it would be possible to improve the electrical properties of GZO films by post-annealing treatment in hydrogen atmosphere [5-8].

2 EXPERIMENTAL DETAILS

In this investigation, the ZnO:Ga thin films were deposited on preheated amorphous glass substrates using P C controlled spray pyrolysis technique supplied by Holmark (Cochin, India). A solution of zinc acetate in a mixed solvent of 75% methanol and 25% double distilled water was used as a precursor. Compressed air was used as the carrier gas. The GZO films were deposited at optimized temperature of 450 ^{0}C by varying the gallium concentration form 1 to 5 at%. The precursor solution was atomized into the fine droplets and carried to the preheated glass substrates.

XRD (Rigaku Mini- II) was used to analyze the crystalline orientation and the crystalline plane spacing of the films. The XRD measurements were performed in a standard θ-2θ scan using a Cu kα radiation (λ = 1.5406 Å) over the range of 200 to 800. The microscopic features were observed through a scanning electron microscope (JEOL-JSM-5600). The acetone sensing properites is studied at 573 K.

3 RESULTS AND DISCUSSIONS

3.1 X-ray diffraction analysis

3.1 X-ray diffraction analysis

The structural properties of Ga doped ZnO thin films produced by the spray pyrolysis method at 450 ^{0}C substrate temperature were investigated by XRD and the results for all doping levels of Ga are shown in Fig. 1. The XRD patterns of these samples are in good agreement with the JCPDS standard (No. 75-0576) data of wurtzite hexagonal ZnO. As seen from Fig. 1, the films exhibit a dominant peak at 2θ = 34.44 corresponding to the (002) plane of ZnO. However, weaker ZnO peaks like (100), (101), (103) and (004) are also observed, suggesting that during the material deposing some grains grow with another orientation [9]. Apart from ZnO characteristic peaks, no peaks that correspond to either gallium, zinc or their complex oxide could be detected. Similar results were also obtained by T. Prasad Rao [10]. This observation suggests that the film do not have any phase segregation or secondary phase formation. Meanwhile, it was apparent that

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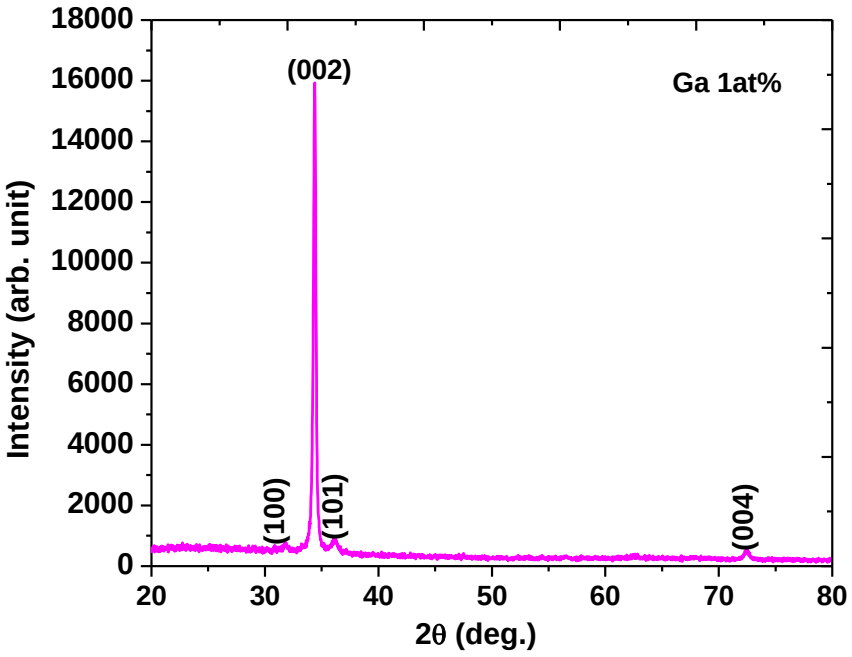
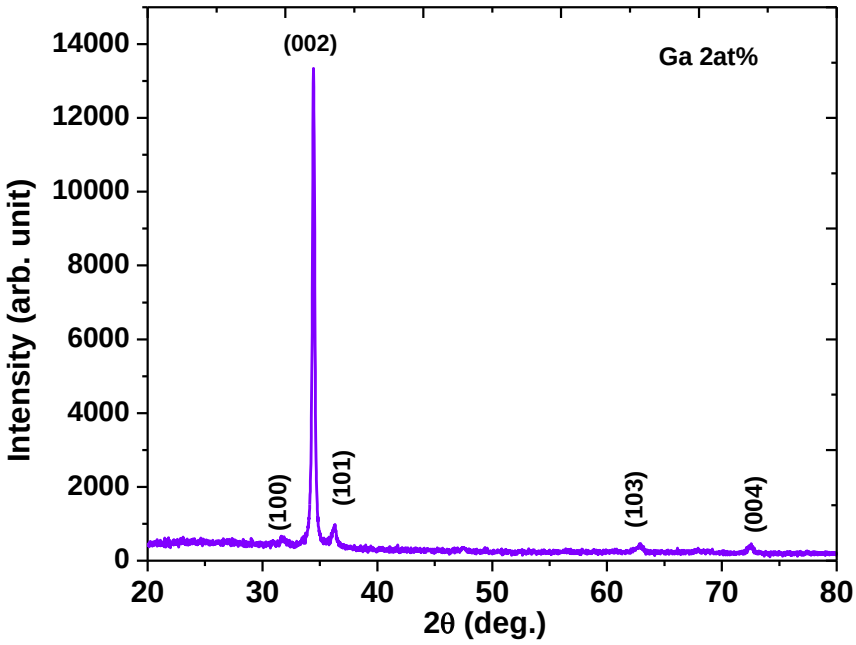


(a)



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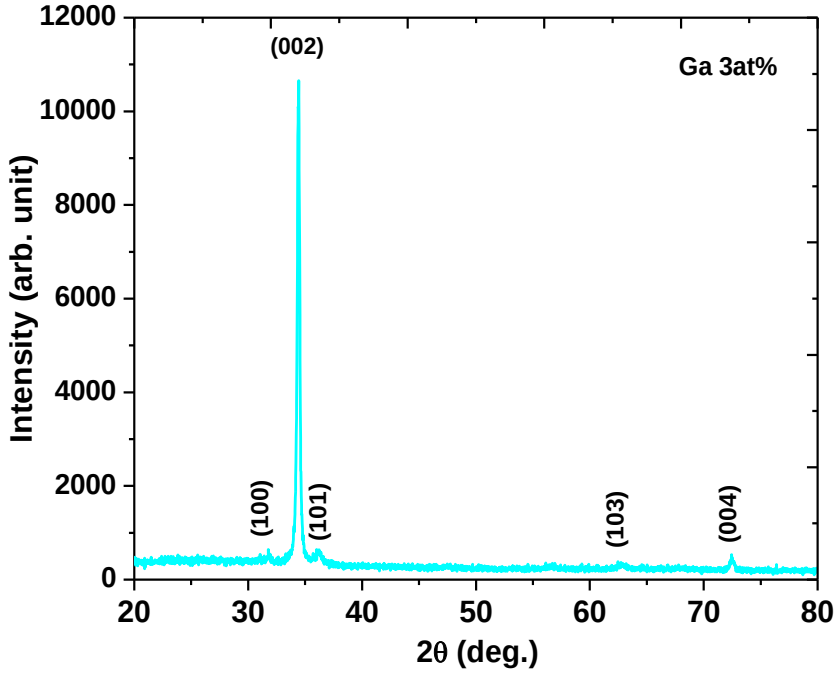

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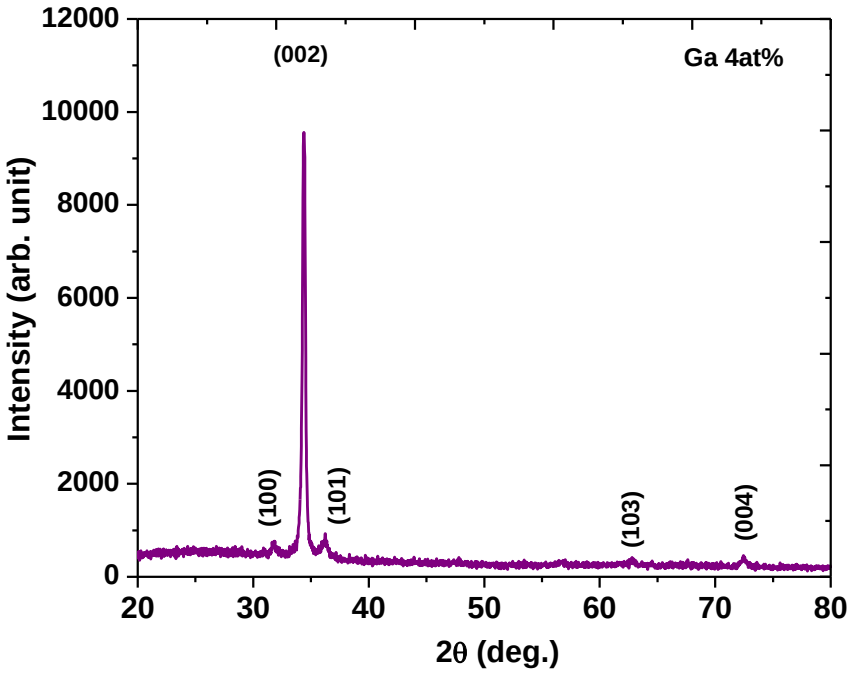

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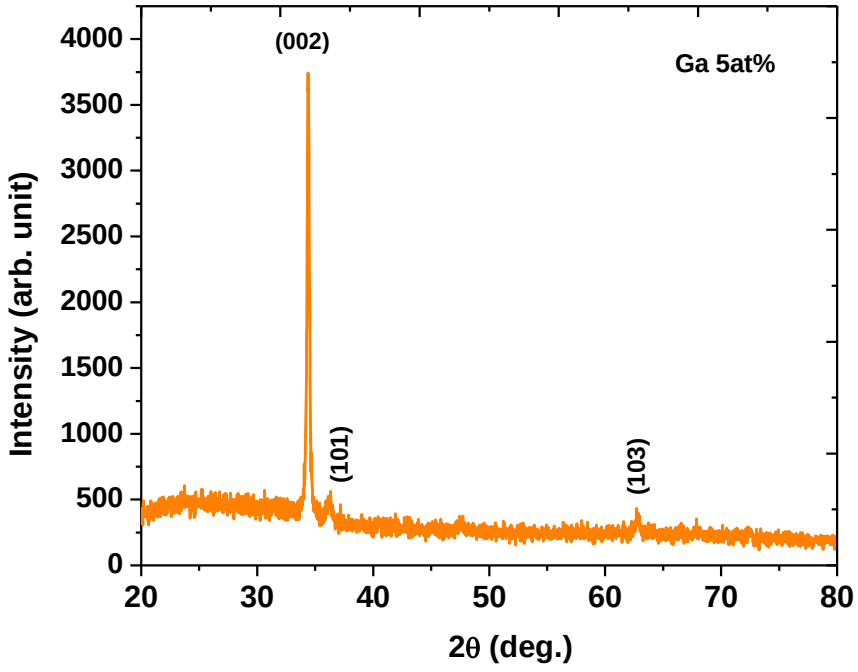


(e)

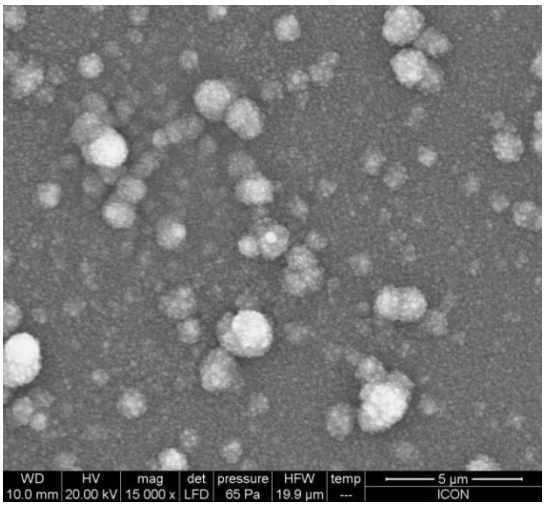
Figure 1: X-ray diffraction spectrum for the ZnO:Ga films with different Ga at%.

intensity of (002) diffraction peak decreased and the full width at half maximum (FWHM) of (002) peak decreased with increase in Ga concentration, indicating that the more the Ga concentration in ZnO films the worse the crystal quality. This might be due to the lattice disorder and strain induced by interstitial Ga atoms of the substitution of Ga for Zn.

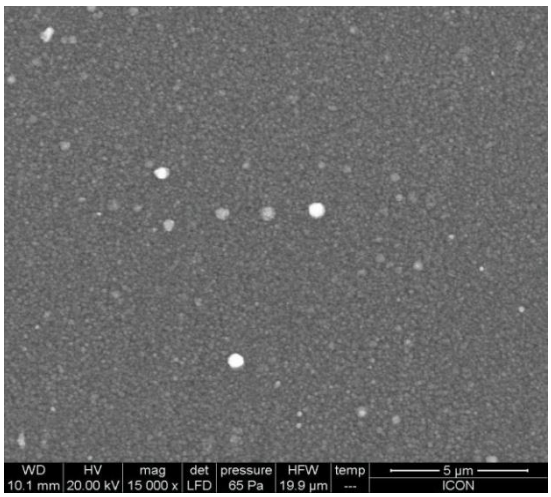
The average crystallite size for (002) peak has been calculated using Deby-Sherrer's equation [11]. It is observed that as Ga doping increases the crystallite size decreased.

3.2. Surface morphological studies

The two-dimensional surface morphologies of as-deposited GZO thin films were carried out using SEM images are shown in Fig. 2. A uniform grain growth in all the film samples is observed from the SEM micrographs. It is also observed that grains are small and distributed uniformly throughout the surface. The uniformity and compactness presented by the films is a result of the specific deposition and solution conditions. In this case, the surface is covered by round and small-size grains, and seems to be a smoother and more uniform surface, whereas, films with a higher content of Ga show an irregular surface, which is covered by different size grains and some big features that seems to be agglomerates of smaller-grains. As Ga doping concentration increases, a



(1at%)



(3at%)

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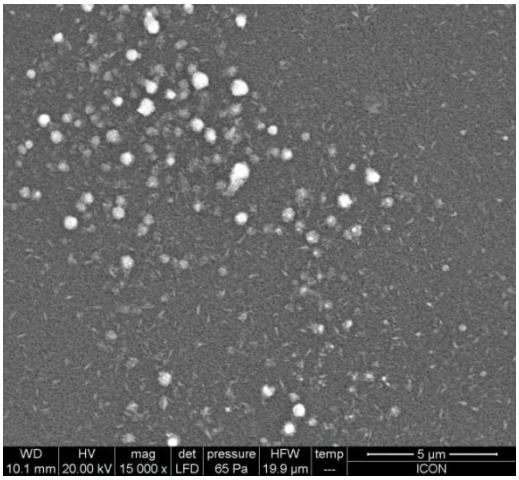
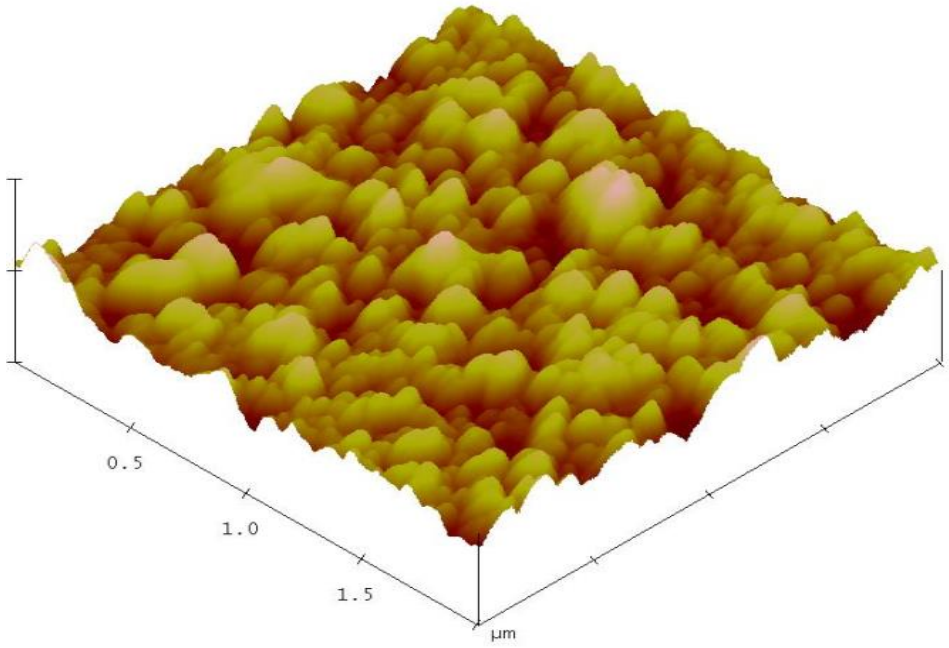


(5at%**)**

Figure 2: SEM micrographs of the GZO films at various Ga at%.

gradual decrease in grain size occurred due to an increasing number of nucleation centers during incorporation of the dopant into the host material [12].

Fig. 3 displays the surface morphology of the corresponding ZnO:Ga thin films revealed by AFM. Although it is impossible to give a direct measure about the actual grain size from the AFM images, the results do exhibit apparent evolution in film grain morphologies with increasing Ga %. Since the films were grown on glass substrates and no epitaxial relation was expected, these phenomena might be understood as a direct consequence of surface diffusion enabled three-dimensional grain growth [13-14]. As seen from the AFM images the surface roughness increases as dopant concentration Ga increases from 1% to 3% and after increase in Ga concentration roughness decreases.



3D AFM image of GZO (1% Ga)

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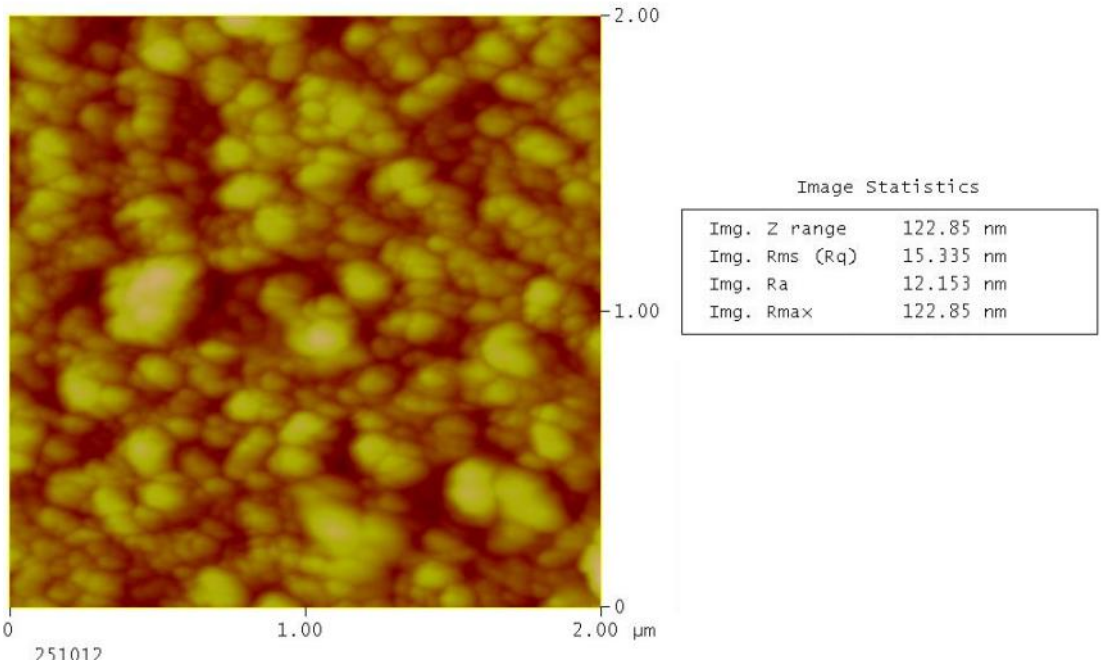

Figure 3 AFM Images 3D and 2D roughness analysis of GZO thin films (Ga 1at%)

3.3 Acetone sensing properties

(a) Effect of temperature and Acetone concentration

Fig. 5.13 shows the response value for Ga-doped ZnO sensors to 1000 ppm acetone at different operating temperature. It can be seen that the response of sensors varies with not only the amounts of the Ga addition but also the operating temperature. All the sensors display a maximum response value at the operating temperature of 573 K. At the optimum temperature, the response to 1000 ppm acetone increased from 15% to 23% as Ga at% is increased from 1 at% to 3 at% and further increase in Ga doping in ZnO response decreased. When the operating temperature increases further, the response value decreases, which may result from the competing desorption of the chemisorbed oxygen. It reveals that the 3 at% Ga-doped ZnO sensor has much higher response value than the other sensors.

Fig. 5.14 shows the gas response as a function of Acetone concentration at 573 K. The figure reveals that the response increased from 12% to 23% as the Acetone concentration increased from 250 to 1000 ppm. However, at higher Acetone concentrations the increase in gas response value was gradual and decreased for Acetone concentrations more than 1000 ppm. The response of a sensor depends on removal of adsorbed oxygen molecules by reaction with a target gas and generation of electrons. An increase in gas concentration increases the surface reaction due to a larger surface coverage.

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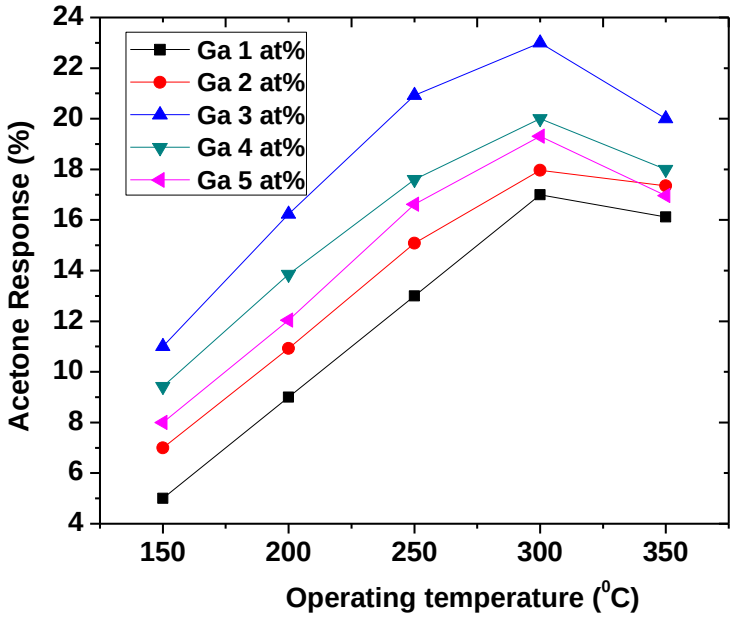

Figure 3: The variation of Acetone response of Ga: ZnO film for different Ga at% to 1000 ppm Acetone at different temperatures.

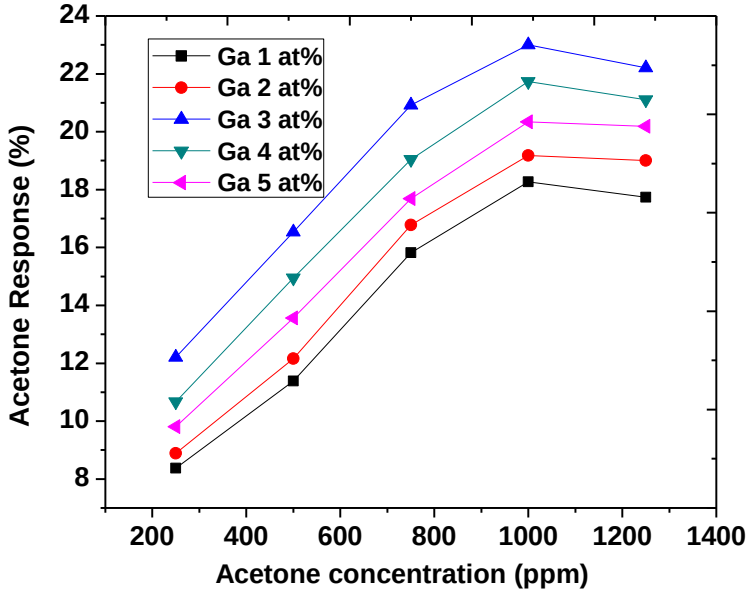

Figure 4: The variation of Acetone response of Ga: ZnO film to different Acetone concentrations

4. CONCLUSIONS

The Ga:ZnO thin films were deposited on amorphous glass substrates using spray pyrolysis technique. The XRD patterns of these samples are of wurtzite hexagonal ZnO. It is also observed from SEM micrographs that grains are small and distributed uniformly throughout the surface. From the AFM images the surface roughness increases as dopant concentration Ga increases from 1% to 3%. The response to 1000 ppm acetone increased from 15% to 23% as Ga at% is increased from 1 at% to 3 at% and further increase in Ga doping in ZnO response decreased.

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