Improving Ammonia Sensitivity on Tin Oxide by Annealing Time Optimization

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Abstract— Tin oxide is one of the most explored thin film materials for gas sensing applications. Sensing properties depend on film's surface morphology which is tuned by either deposition parameters or by annealing considerations. This work explores the importance of annealing time to get optimum sensing response for tin oxide film. Samples annealed for 1-5 hours were examined for electrical resistance, surface morphology and gas sensing behavior (10 ppm ammonia). The optimized annealing time is found to be 3 hours at 350°C based on the sensor response and stability over a period of 15 days.

Keywords: Tin oxide, Annealing time, Gas sensing, Electrical resistance.

1 Introduction

TIN OXIDE is being extensive investigated for gas sensing applications [1-2]. Tin oxide surface morphology decides its response for gas sensing [3]. Surface morphology of the material is dependent on the deposition parameters and post deposition treatments such as annealing. Annealing of tin oxide is also widely studied; however, there is limited information available on annealing duration at fixed temperature. In this work, annealing time is optimized for annealing in air ambient at 350°C. Annealing is important as it removes crystallographic defects and oxygen vacancies if any. Also the required crystallographic changes can be made with controlled annealing in air. Sputter deposited tin oxide is generally found to be in amorphous phase, which is not very stable and sensing performance degrades rapidly. To achieve a stable crystallographic phase, annealing plays an important role.

2 Aim for the study

This study aims to develop an annealing protocol to realize tin oxide sensing films for reliable and stable gas sensing application. It is important to explore the annealing duration as it is related to the process cost and sensor performance. The film annealed for longer time adds to the fabrication cost; on the other hand, if sample is annealed for lesser period, the sensor performance gets compromised.

3 Methods

For the current study, 7 sets of 3 samples each are prepared having sensing film on interdigitated electrodes (IDE). Silicon wafers are first piranha cleaned followed by 0.5μm thermal oxidation. Silicon dioxide provides the electrical isolation between substrate and IDE. Wafers are then patterned for IDE using photolithography, DC sputtered Ti (200Å)/ Pt (1300Å) followed by lift-off process. After IDE, tin oxide sensing film is realized using same deposition and lift-off approach. Tin oxide deposition was carried out by reactive sputtering of tin with 60:40 ratios of Ar and O_2. Wafers are finally diced and the chips are packaged in flat ceramic packages. Fig. 1 shows the patterned platinum interdigitated electrodes and sensing film on it. Complete process of gas sensor fabrication has been published elsewhere [4].

Samples thus prepared are annealed at 350°C for 0 to 5 hours. Each sample was evaluated electrically using DC probe station, physically by atomic force microscopy (AFM) and for sensing response using controlled exposure of ammonia (NH_3).

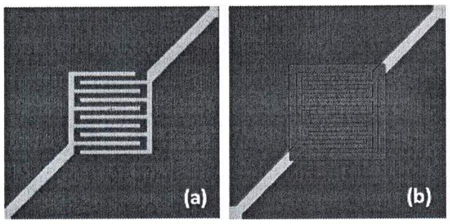

Fig. 1. Patterned platinum electrode formation and tin oxide sensing film deposited over it

4 Results

Differently annealed samples are characterized electrically, physically and for gas sensing as mentioned above. The surface morphology does not show significant changes; hence only one image of the film annealed at 350°C has been shown in fig. 2. Surface morphology of the film depicts the granular surface with an average grain size of 35nm. Granular surface is always preferred for sensing purpose due to increased surface area. The five sets of samples were further characterized for electrical resistance to understand the changes in resistance with the change in annealing time. It was observed that the initial resistance of the samples was very high (100s of GΩ), which is expected due to amorphous structure of as-deposited film. On annealing the resistance increased till 1.5 hours and then decreased drastically and got almost stable in a particular range (fig. 3). This sharp change in resistance is quite interesting and can be related to a stable phase change from amorphous film. Initial increase in resistance is the evidence of oxidation of tin.

The samples are then characterized for gas sensing (10 ppm ammonia). Response for the same is shown in fig. 4. It is observed from the curve that the sensor response is higher initially, decreases subsequently and again increases after 2.5 hours of annealing. The response can be explained by the fact that the film has defects initially leading to more response, which decreased subsequently and once the suitable crystallographic phase is achieved the response again increased. Further annealing doesn't show significant change in response. Hence, it may be inferred that the film so deposited should be annealed for at least 3 hours for stable sensing behavior. Stability is verified by exposing the sensors every day for 15 days (fig. 5) and it was found that the sensors annealed for more than 3 hours are more stable with lesser response variation (min to max).

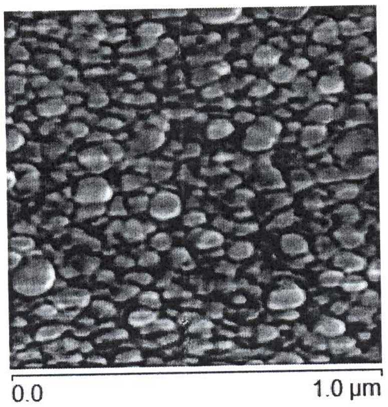

Fig. 2. Atomic force image of the sputtered SnO_2 film

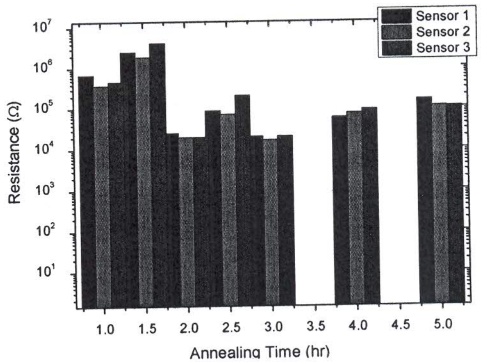

Fig. 3. Electrical resistance of the samples annealed at 350°C for 1-5 hours

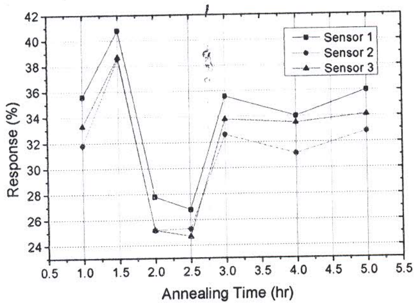

Fig. 4. 10 ppm Ammonia responses for the samples annealed at 350°C for 1-5 hours

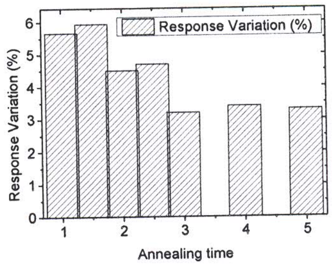

Fig. 5. 10 ppm Ammonia responses for the samples annealed at 350°C over 15 days

5 Conclusion

For optimized sensing performance, annealing temperature as well as annealing time needs to be optimized. As deposited DC sputtered tin oxide films are amorphous and exhibits very high electrical resistance. Electrical resistance decreased significantly after annealing for >1.5 hours at 350°C. For stable gas sensing response, annealing >3 hours is important. The stability of the same was checked over a period of 15 days.

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