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Laser sintering ZnO thick films for gas sensor application

Bai Lin Zhu · Chang Sheng Xie · Ai Hua Wang · Jun Wu · Run Wu · Jing Liu

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Abstract The thick films based on ZnO nanoparticles were prepared by laser sintering with different powers and sintering times for the first time. The microstructure of laser-sintered films was observed by SEM, and their resistance and sensitivity to VOCs as a function of temperature were measured, and compared with the unsintered thick films. The results showed that the laser-sintered ZnO thick films had higher sensitivity than that of the unsintered films. In all the laser-sintered ZnO thick films, the films sintered at shorter sintering time had the higher sensitivity at the same power, and the sensitivity of the films could be further improved with increasing laser power from 60 to 70 W. The differences in resistance and sensitivity were probably due to the fact that the microstructure of the films and stoichiometric proportion of ZnO changed with the laser power and sintering time.

Introduction

The thick films for gas sensor are usually sintered at a certain temperature, and the hot-resource commonly used for sintering is provided by electronic resistance furnace. The effect of sintering temperature and time on the sensitivity of films had been discussed [1]. However, few works concerned with new hot-resource and technique (e.g. pulsed sintering) for sintering was reported. Laser sintering had been applied in metal, ceramics and composites [2–4], but its application in preparing films for gas sensor was attempted in this study for the first time. Using laser sintering, the fabrication parameters are easily adjusted and the sintering time is greatly shortened, which make it is possible to screen the materials with the best gas-sensing properties. Furthermore, laser beam can be accurately located, and the selected sintering is facilely carried out, that is the sintering parameters for single one in sensor array can be freely controlled, resolving the problem that the sintering parameters for single one are inconsistent during preparing sensor array by conventional sintering method. In this paper, using ZnO nanoparticles as raw materials, the effects of laser parameters (output power, sintering time) on the microstructure, resistance and the sensitivity of the films were investigated.

Experimental procedure

ZnO nanoparticles, the basic functional materials, were prepared by vapor-phase oxidation with metallic zinc as raw materials in a gas mixture of Ar + O_2 at a pressure of 1.0×10^4 Pa, where the oxygen partial pressure was kept at about 2×10^3 Pa by controlling the oxygen flux. The obtained ZnO nanoparticles show rod shape with 20~50 nm in width and about 150 nm in length and needle shape with 5~10 nm in diameter and about 200 nm in length. The pastes of ZnO were formed by adding suitable amount distilled water, and then they were coated on one side of Al_2O_3 tubes (4 mm in length, 1.2 mm in external

B. L. Zhu (✉) · J. Wu · R. Wu · J. Liu
Key Laboratory of Hubei Province for Ceramics and Refractories or Nanomaterials Center, Wuhan University of Science and Technology, Wuhan 430081, P.R. China
e-mail: zhubailin97@hotmail.com

C. S. Xie · A. H. Wang
Department of Materials Science and Engineering, Huazhong University of Science and Technology, Wuhan, Hubei 430074, P.R. China

diameter and 0.8 mm in internal diameter) on which Au electrodes and Pt wires had been fixed at each end. The thick films were dried in air to remove water and then were fired by laser beam produced by 400 W-Nd:YAG (JH-VI) laser. The laser power used was 60 and 70 W, and the sintering time varied from 9 to 45 s. In order to comparison, some films dried in air did not further sinter by laser. A small Ni–Cr alloy coil with the resistance of about 33 Ω was placed through the tubes as a heater.

In order to improve their stability and repeatability, the films were powered at 320 °C for 7 days in air before electrical resistance in air and gas-sensing studies were carried out. The temperature of films was varied from 190 to 450°C by adjusting the heating power. The experimental procedure was described in detail in the literature elsewhere [5]. After the resistance and gas-sensing measurements, the surface morphologies of thick films were observed by a scan electron microscope (SEM, XL30TMP). The gas sensitivity, S, is given by $S = R_a/R_g$, where R_a and R_g express the resistance of the sensor in air and in detecting gas, respectively.

Experimental results and discussion

Figure 1 shows the surface morphologies of unsintered films and films sintered by laser beam with output power of 60 W. It is observed that grain size of all the films is not obvious different (about 250–350 nm), somewhat larger than that of nanoparticles, but grain morphology in thick films is similar to that of nanoparticles. Compared the unsintered films with the laser-sintered films, it is found that the unsintered films have much bigger pore, and the grains are contacted randomly. After laser sintering, the bigger pore decreases and the agglomerations, which are formed by connecting some small grains together, appear at the same time. It is obvious that the laser-sintered films exhibit higher compactness than that of the unsintered films, and the compactness increases with increasing sintering time. As similar as the films sintered at 60 W, SEM observations (Fig. 2) show that the compactness of films sintered at 70 W gradually increase with increase in sintering time, but the grain size is more uniform and the bigger pore decreases.

The relation of sensitivity of the films and operating temperature is shown in Fig. 3, indicating that the sensitivity is dependent on output power and sintering time. Compared with the unsintered films, the laser-sintered films have higher sensitivity. It is well known that the sensitivity is deeply related to the microstructure of the ZnO films, i.e., the grain size (D), the neck size (X) and the depth of the surface space-charge layer (L) [6]. The sintered necks between grains in unsintered thick film do not effectively form due to the fact that the films have been heated only during the aging and measurement. Thus, the grain-boundary contacts dominate the electrical resistance and the gas sensitivity of the unsintered films (grain

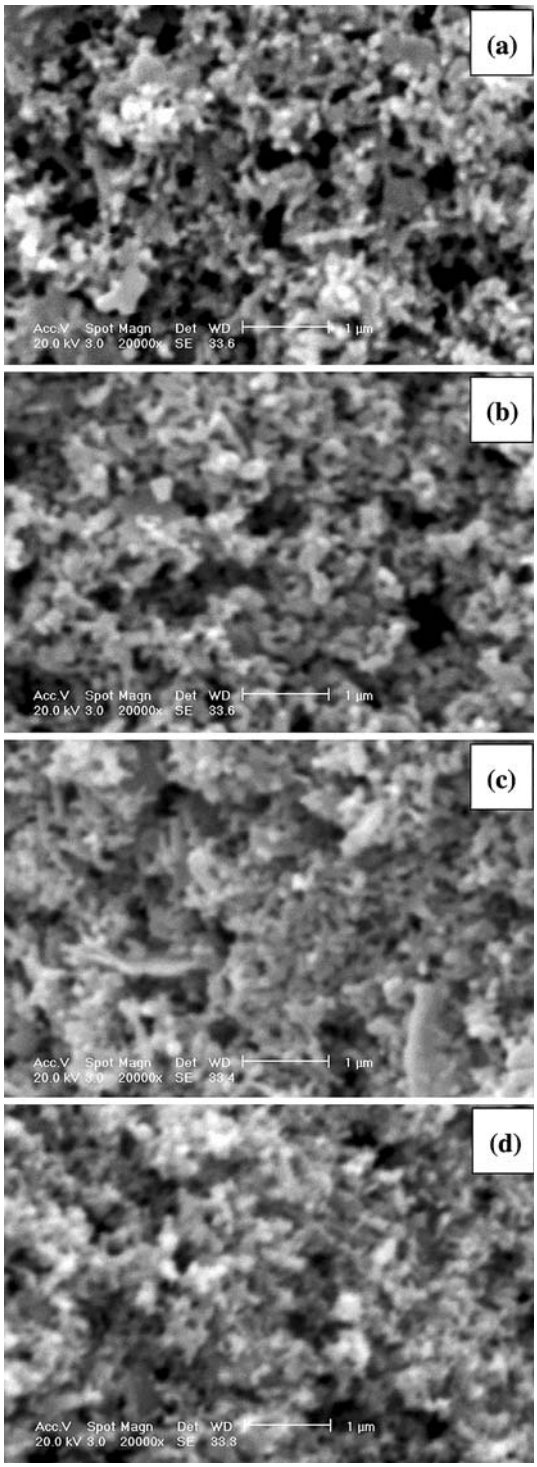

Fig. 1 The SEM images of unsintered and laser-sintered ZnO thick films at 60 W with different times (**a**) unsintered; (**b**) 9 s; (**c**) 27 s; (**d**) 45 s

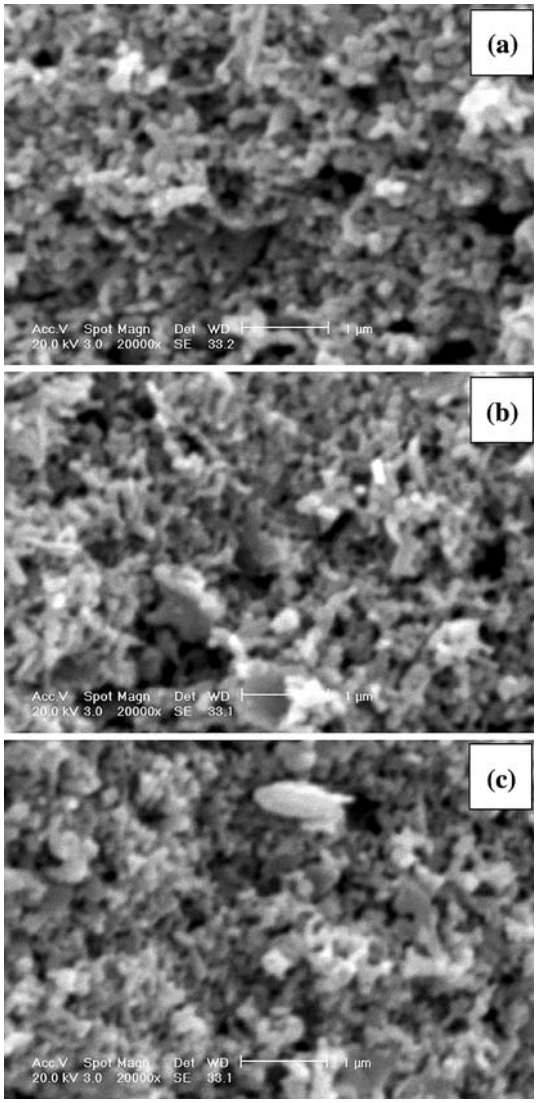

Fig. 2 The SEM images of ZnO thick films sintered by laser beam at 70 W with different sintering times (**a**) 9 s; (**b**) 27 s; (**c**) 45 s

boundary control). After laser sintering, the sintered necks between grains form and become the most resistive part and thus control the gas sensitivity of the films (neck control). As mentioned above, the grains size of all the films is not obvious different, and the size of necks is usually smaller than that of grain. Obviously, the size of necks is more comparable to 2 *L*, thus the sensitivity of neck controlled films is drastically promoted, i.e., the films sintered by laser have higher sensitivity than that of unsintered films.

From the Fig. 3, the maximal sensitivity is observed at sintering time of 9 s, and the sensitivity decreases with increase in sintering time at the same power. Furthermore, it is worth noting that the sensitivity of the films sintered at 70 W is markedly higher than that at 60 W, and the optimum sensitivity temperature of the films sintered at 70 W is lower than that at 60 W. The films become compact with sintering time as mentioned above, which implies the specific surface area of the films decreases and sintered neck size increases, so the sensitivity of the films decreases with increasing sintering time. However, it is difficult to explain why the sensitivity of the films at 70 W is significantly higher than that at 60 W in according to the changes in specific surface area of films or sintered necks size. In order to further explain the difference in sensitivity, the resistance of films as a function of temperature was also measured, as shown in Fig. 4.

From the Fig. 4, the resistance of the unsintered films is higher than that of laser-sintered films, which is related to decrease in conductivity channels in incompact films. At the output power of 60 W, the resistance of films at 9 s is lowest, and it increases with increasing sintering time to 27 s. As the sintering time further increases to 45 s, the resistance decreases but it is higher than that at 9 s. When the output power is 70 W, the resistances of films shows increased trend with sintering time. Usually, the resistance of films decreases with increase in the compactness of films because the amount of chemisorbed oxygen that causes the resistance increase decreases and the conductivity channels increases. However, the resistance of the films increases with the sintering time at same power, as mentioned above. It is also found that the resistance of the films sintered at 70 W is lower than that at 60 W at all the sintering time from the Fig. 4. These changes of resistance may be related to the changes of stoichiometric proportion of ZnO during laser sintering, i.e., the changes of the ratio of interstitial Zn atoms will cause the changes of carrier concentration, and further influence the resistance of films. In conclusion, the resistance of films depends on two factors: the compactness and carrier concentration of films. When the sintering time increases from 9 to 27 s, the dominative factor is the decrease of carrier concentration, which is caused by laser ablating interstitial Zn atoms, thus the resistance increases with the sintering time. When the laser power is 60 W, only the interstitial Zn atoms is ablated. Once the power increases to 70 W, zinc and oxygen atoms may be ablated simultaneously by laser, finally the ratio of interstitial Zn atoms in films is higher that at 60 W, thus the resistance of films sintered at 70 W is lower than that at 60 W. The carrier with high concentration not only decreases the resistance of films, but also enhances the chemisorbed oxygen [7], thus the sensitivity of the films is greatly improved when the laser power increases from 60 to 70 W. At the same laser power, the decrease of sensitivity with sintering time maybe also results from the decrease in carrier concentration in addition to the increase in films compactness and sintered necks size as mentioned above.

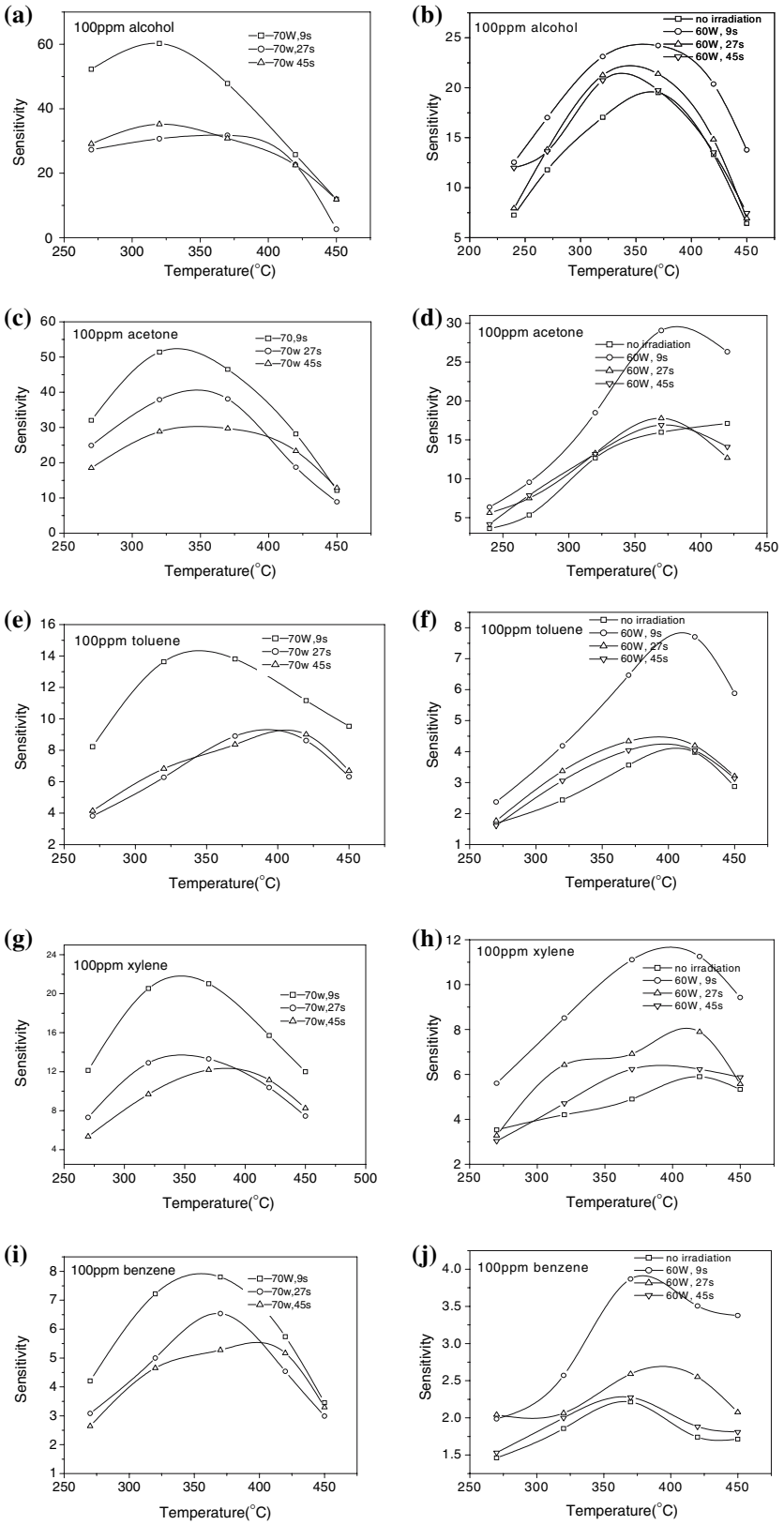

Fig. 3 The sensitivity of unsintered and laser-sintered ZnO thick films as a function of operating temperature

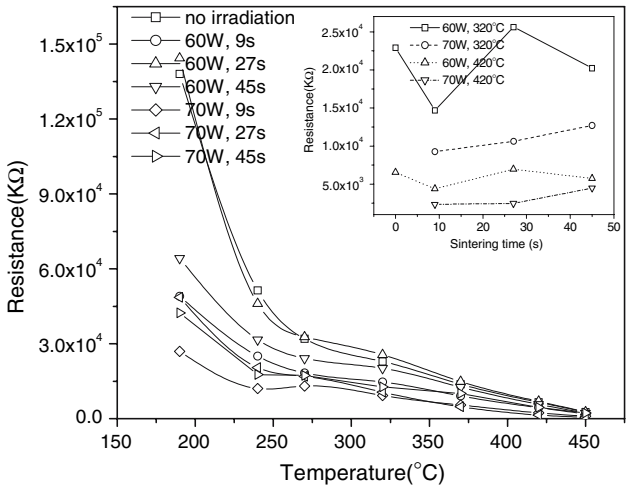

Fig. 4 The resistance of unsintered and laser-sintered ZnO thick films as a function of operating temperature. The inset shows the dependence of the resistance on the sintering time at different operating temperatures

It is found that the film cannot be sintered on the alumina substrate when the laser power is slightly higher than 70 W during experimental process. This is because when the adsorbed energy of the films is high beyond the gasified energy of powder, no new powders compensate the powders removed by gasifying and explosion under the laser beam, finally sintered films cannot be performed. It is obvious that 70 W is threshold power for laser sintering ZnO thick films. At this power, the gas-sensing properties of films are attributed to the change in stoichiometric proportion of ZnO and the microstructure of films during the laser sintering process.

Conclusions

Laser-sintered ZnO thick films have lower resistance and higher sensitivity than that of unsintered films. Their resistance and sensitivity are dependent on output power and sintering time. The sensitivity of thick films at 70 W is obviously higher than that at 60 W, and their resistance is lower than that at 60 W. At the same power, the sensitivity decreases and the resistance increases with increasing sintering time. These changes of resistance and sensitivity with power and sintering time may be related to the changes in stoichiometric proportion of ZnO and the microstructure of films during the laser sintering process.

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