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Response characteristics of Sn doped Zinc Oxide (Sn:ZnO) thin films to ethanol vapour

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Abstract

Sn doped zinc oxide (Sn:ZnO) thin films have been prepared under different doping concentrations(0-1.5 at%) by spray pyrolysis technique. The structural and optical properties of the films are explored and then tested for ethanol sensing. Exposure of ethanol vapour decreases the resistance of undoped and doped films. The response of the film is measured for both ZnO and Sn:ZnO films at different operating temperature (225-350^{0}C) and concentration of ethanol in air. It is observed that Sn doped ZnO films are more sensitive to ethanol vapour than undoped ZnO film. In this work maximum sensitivity (68.51%) is observed for 0.5 at% Sn:ZnO film for 500 ppm of ethanol at 573 ^{0}K. Again with the increase in doping concentration, the sensitivity of the film is found to be decreased. Further all the films have shown faster response and recovery times at higher operating temperatures.

Key words: Sn:ZnO thin film, spray pyrolysis, ethanol ,sensor

1. Introduction

Studies of semiconductor oxides are growing very rapidly because of the successful production of these thin film materials as detecting devices. In the recent years, there has been great demand for ZnO films because they can be made to possess high electrical conductivity, high infrared reflectance and high visible transmittance. Low resistive zinc oxide films have been achieved by doping with different Group III elements like aluminium, boron, indium, gallium or with Group VI elements like fluorine. [1-8]. The electrical resistivity change of semi conducting material upon exposure to reducing gases/ vapors is used for various gas detection. The sensing capability is due to the surface properties involved in the reaction mechanism with the gas/vapor to be detected [9,10]. Zinc oxide (ZnO) thin films are attractive in the semiconductor fields for gas sensor applications because of its chemical sensitivity to volatile and other radical gases, its high chemical stability, suitability to doping, non toxicity, abundance in nature and low cost. Apart from the sensing applications, thin films of ZnO find many promising applications such as transparent electrodes, surface acoustic wave devices, heat mirrors etc.

Many researchers have studied doped and undoped ZnO thin films for the detection of toxic and inflammable gases [11-14]. Paraguay et al [15] had studied the influence of Al, In, Cu, Fe and Sn dopants on the response of thin film ZnO gas sensor to ethanol vapour. Lucio-Lopez et al [16] prepared In-doped ZnO thin

films by chemical spray and studied its structural, optical, morphological and electrical properties. Sprayed ZnO thin films for ethanol sensors have been investigated by Sahay et al. [17]. This material has been investigated in the form of single crystals [18], sintered pellets [19], thick films [20], thin films [21] and heterojunctions [22]. Joseph et al had studied the chemical spray deposited Al- doped ZnO thin films to study its structural, electrical and optical properties. [23]. Different deposition techniques have been widely used for the preparation of semiconducting thin films. However, a technique, which is the most reliable and economic, is the main goal. Among the most studied techniques are the chemical vapor deposition, radio frequency magnetron sputtering, sol-gel technique and spray pyrolysis technique. In this work, we have investigated the optical and electrical properties of Sn(Tin)-doped zinc oxide (ZnO) thin films prepared by spray pyrolysis technique and finally the sensing behavior of these films towards ethanol is studied, as exposure of ethanol vapor to human beings is harmful.

2. Experimental

Tin doped zinc oxide (Sn: ZnO) thin films are deposited on to the glass substrates, which are cleaned with freshly prepared chromic acid, detergent solution and distilled water. The schematic representation of the spray system is described elsewhere [24]. The deposition method involves the decomposition of a solution of 0.1 M concentration of high purity zinc acetate dehydrate (Merck, India) prepared in distilled water. The dopant concentration (Sn/Zn at%) is varied from 0 at% to 1.5 at%. The compound source of dopant is stannic chloride penta hydrated ($SnCl_4$. $5H_2O$; Merck, India). The resulting solution is subsequently sprayed onto heated substrate at a constant temperature of (410 ± 20 ^{0}C), which is monitored by a chromel alumel thermocouple fitted close to the substrate with the help of a Motwane Digital Multimeter (Model: 454). The atomization of the solution into a spray of fine droplets is affected by the spray nozzle with the help of compressed air as carrier gas.

The thickness of the films is determined by the weight difference method using an electronic precision balance (Citizen, model: CY 204). Structural analysis of the films is carried out using a PANalytical X'Pert Pro X-ray diffractometer with CuKα radiation (λ = 1.5418 Å) as an X-ray source at 40kV and 30mA in the scanning angle (2θ) from 30 to 70^0 with a scan speed 0.02^0/ s. The optical transmission spectra of the films are obtained in the UV/VIS/near IR region up to 1100 nm using Perkin Elmer UV-VIS spectrometer (Model: Lamda 35). For making ohmic contacts at both the ends of the film, high conducting silver paste is used and is dried at a temperature of 150^{0}C. The film is mounted on a home made two-probe assembly placed inside a silica tube, which is inserted co-axially inside a resistance-heated furnace. The electrical resistance of the film is measured before and after exposure to ethanol using a Keithly System Electrometer (Model: 6514).

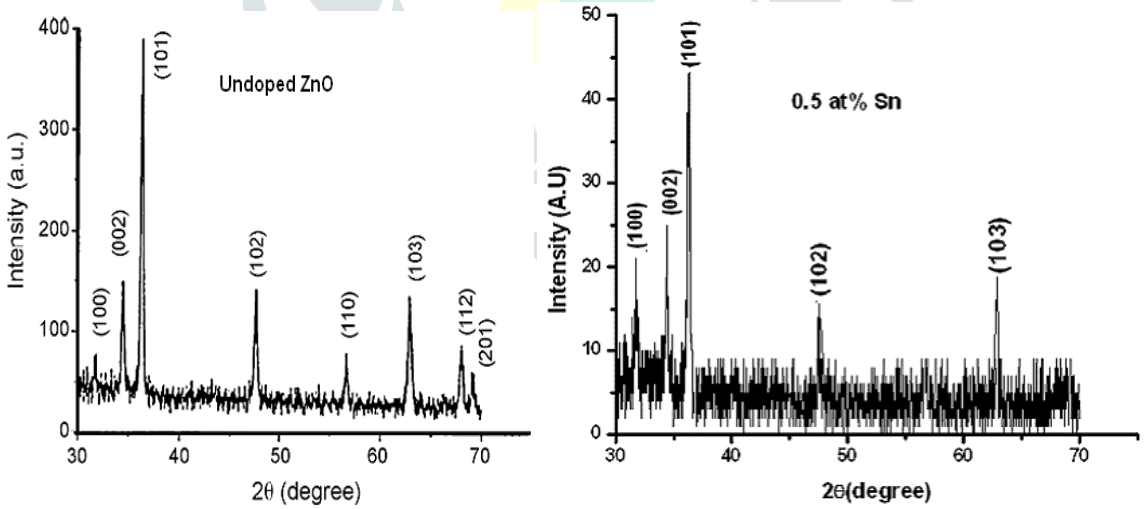
Spray parameters	Optimum value/ Item
Nozzle	Glass
Nozzle- Substrate distance	45 cm
Solution concentration	0.1 M
Solvent	Distilled water
Dopants solution	$SnCl_4$. $5H_2O$
Solution flow rate	6 ml/ min
Carrier gas	Compressed air
Gas pressure	4 kg/cm^2
Substrate temperature	(410 ± 20) ^0C

Table 1: Process parameters for the deposition of films.

3. Results and discussion.

3.1. Structural analysis

Fig. 1 shows the X-ray diffraction patterns of the typical Sn-doped ZnO films.



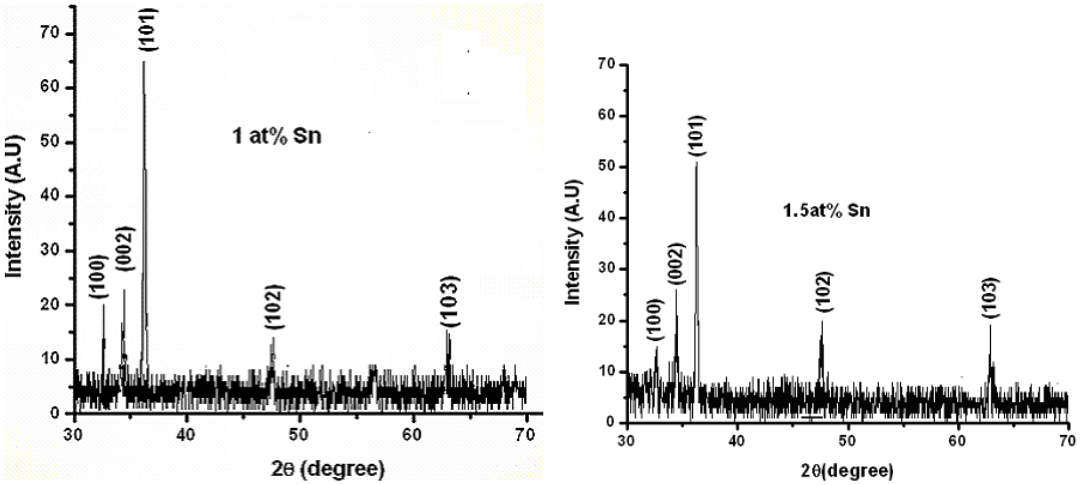


Fig.1. XRD patterns of the typical Sn-doped ZnO thin films

All the films are found to be polycrystalline in nature, possessing "hexagonal wurzite" structure as per ICDD reference pattern (01-070-8070). No phase corresponding to tin or other tin compound is observed in the XRD patterns, which indicates a low level incorporation of tin in ZnO film[20]. All the Sn-doped ZnO films show the most intense peak corresponding to (101) plane while the other planes corresponding to (100), (002), (102), (103), etc, are present with low relative intensities. The crystallite size of the films is calculated using Debye-Scherrer equation.

$$D = \frac{0.9\lambda}{W\cos\theta} \quad \text{---------- (1)}$$

It is observed that the crystallite size of 0.5at% Sn-doped ZnO film is less than that of undoped ZnO of similar thickness. This is due to the lesser ionic radius of Sn^{+4} (R_{Sn}^{+4} = 0.071 nm) which substitutes Zn^{+2} (R_{Zn}^{2+} = 0.074 nm), thereby decreasing the crystallite size. However, crystallite size does not vary systematically with Sn dopant concentration, which is attributed to the lattice disorder produced in the films at higher dopant concentrations due to the difference in their ionic radii [17].

3.2. Optical studies.

The optical absorption spectra of the ZnO:Sn films with different Sn dopant concentration (0 to 1.5 at %) as a function of wavelength are shown in figure 2. It is evident from the figure that the films grown under the same process parameter have low absorbance in the visible/near infrared region while the absorbance is high in the ultraviolet region. Further a steep rise in the absorbance near the absorption edge is observed for all the doped films that hint at a direct type transition.

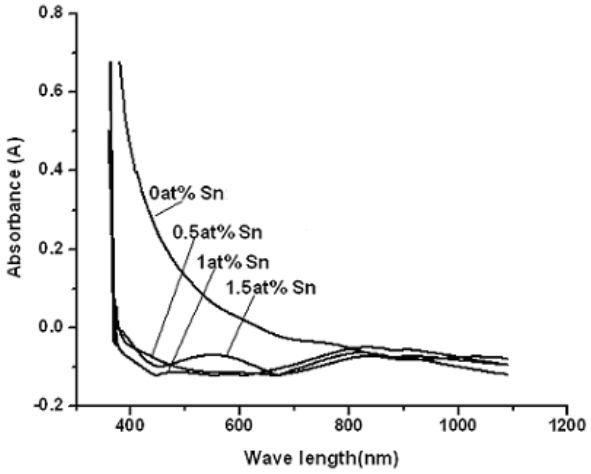


Fig.2. Absorbance spectra of undoped and Sn-doped ZnO thin films

The absorption coefficient (α) is calculated using Lambert law as follows [19].

$$\text{Ln}\left[\frac{I_o}{I}\right] = 2.303\,A = \alpha\, d \quad \text{----------} \quad (2)$$

where I_o and I are the intensity of incident and transmitted light respectively, A is the optical absorbance and d the film thickness.

The absorption coefficient (α) was found to follow the relation----

$$\alpha = \frac{[\,A\,(h\nu - E_g)^{n/2}\,]}{h\nu} \quad \text{----------} \quad (3)$$

Where A is a constant and E_g is the optical band gap.

Plots of $(\alpha h\nu)^2$ versus photon energy (hv) in the absorption region near the fundamental absorption edge is shown in fig.3. In this case n = 2 gives the best linear graph which indicates direct allowed transition in the film material.

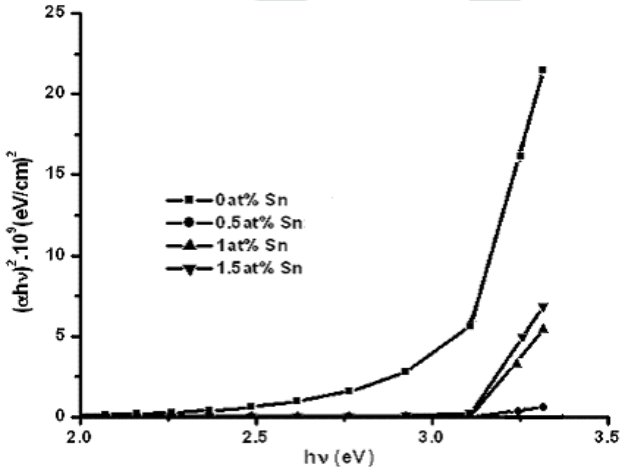


Fig.3. Plots of $(\alpha h\nu)^2$ vs hv for different Sn-doped ZnO thin films.

The optical band gap, estimated by the extrapolation of the linear region of the graph to the photon energy axis is found to be increasing from 3.02 eV to 3.13 eV with Tin (Sn) dopant concentrations from 0 to 1.5 at%. The change in band gap can be attributed due to the Burstein-Moss band gap widening and band gap

narrowing due to electron-electron and electron-impurity scattering [20]. The variation of band gap with Sn doping concentration is listed in table 2.

Film examined	Optical band gap (eV)
0 at% Sn-doped ZnO	3.02 ± 0.01
O.5 at% Sn-doped ZnO	3.09 ± 0.01
1 at% Sn-doped ZnO	3.11 ± 0.01
1.5at% Sn-doped ZnO	3.13 ± 0.01

Table2.Variation of band gap with Sn dopant concentrations.

3.3 Ethanol sensing characteristics of Undoped ZnO film

The sensing characteristics of undoped ZnO film as a function of the operating temperature for three different concentrations (100, 300, and 500 ppm) of ethanol in air is represented in fig4. The sensitivity of the films was determined using following equation, as ethanol possesses the reducing behavior.

$$S = \frac{(R_a - R_g)}{R_a} \times 100\ \%$$

where R_a is the resistance of the film in air and R_g is that upon exposure to ethanol.

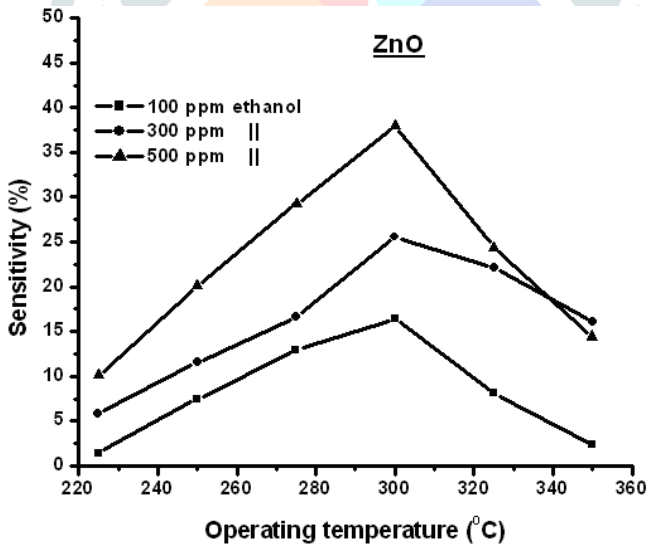


Fig.4. Response characteristics of ZnO film as a function of operating temperature for three different concentrations (100, 300 and 500ppm) of ethanol in air

It is seen that for each concentration of ethanol in air, the response of ZnO film increases up to 300^0C and then decreases with further increase in temperature. It is obvious from the figure that operating temperature plays a vital role in determining the response of the film. There exists an optimum operating temperature of a sensor to achieve the maximum response to a gas. [11]. Also, the adsorption of atmospheric oxygen on the film surface depends upon the operating temperature [12]. At a low operating temperature, the response of the films to ethanol is restricted by the speed of the chemical reaction because the gas molecules do not have enough

thermal energy to react with the surface adsorbed oxygen species. At higher operating temperatures the thermal energy obtained is high enough to overcome the potential barrier and thus the electron concentration increases significantly due to sensing reaction, which in turn leads to an increase in response of the film. At temperatures higher than 300^0C, the adsorbed oxygen species available at the sensing sites on the film surface are not enough to react with ethanol molecules. This results in a small change in resistance at higher temperatures, which in turn leads to a decrease in response [10]. It is further observed that the sensitivity increases with an increase in ethanol concentration. The film shows a maximum sensitivity (~38 %) at 300^0 C to 500 ppm of ethanol in air.

3.3.1 Influence of Sn dopant to the response characteristics

The sensing characteristics of Sn-doped ZnO films as a function of the operating temperature for three different concentrations (100, 300, and 500 ppm) of ethanol in air is shown in fig.5.

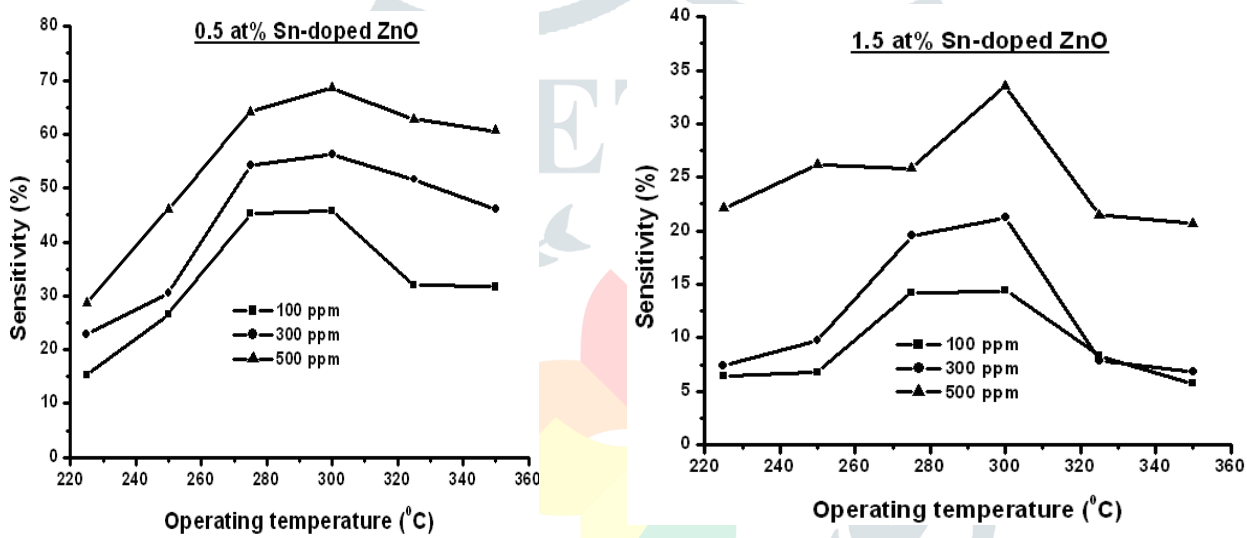


Fig.5. Sensitivity Vs operating temperature of 0. 5at% & 1.5 at% Sn-doped ZnO films for three different concentrations (100, 300 and 500ppm) of ethanol in air.

It is observed in the figure that compared to undopd ZnO film, Sn-dopant increases the sensitivity of the film towards ethanol vapour. A maximum sensitivity of 68.51% is observed in case of 0.5 at% Sn-doped ZnO film to 500 ppm of ethanol at 300^0C, which is much greater than that of undoped ZnO films. Further with an increase in Sn doping concentration, the sensitivity is found to be decreasing. It may be due to the due to the disorder produced in the lattice at higher doping concentration due to the difference in the ionic radii of Zn^{+2} and Sn^{+4} as reported earlier[29].

3.3.2. Variation of response with ethanol concentration

The sensitivity of 0.5 at% Sn-doped ZnO film as a function of ethanol concentration in air at different operating temperatures is shown in fig.6.

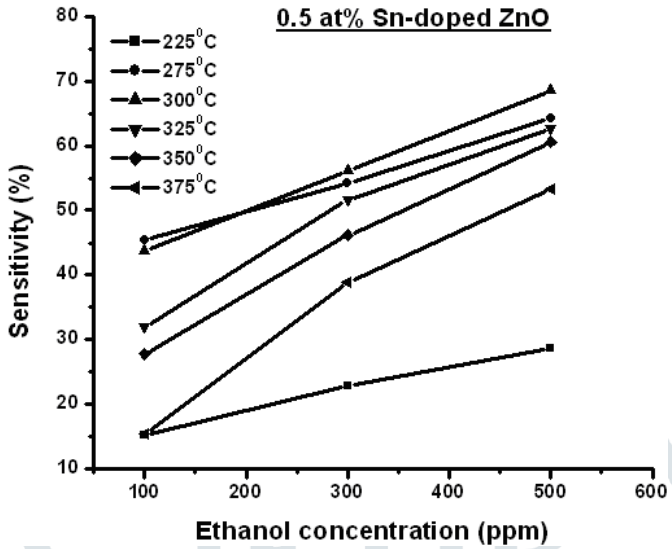


Fig.6. Sensitivity Vs ethanol concentration of 0.5 at% Sn-doped ZnO film at various operating temperatures.

It is observed that, at a particular temperature, the sensitivity increases more rapidly at lower ethanol concentration than that at higher concentration. This indicates that at higher concentration, the surface coverage of ethanol molecules on the film begins to attain saturation which results to a comparatively slower increase in sensitivity. Further, a linear increase in response with ethanol concentration is observed at 275^{0}C and 300^{0}C. This may be due to the availability of sufficient adsorbed ionic species which reacts most effectively at these temperatures.

3.3.3. Transient response characteristics

The transient response characteristics of 0.5 at % Sn-doped ZnO films for various ethanol concentrations (100, 300 and 500 ppm) in air at 300^{0}C is shown in fig.7.

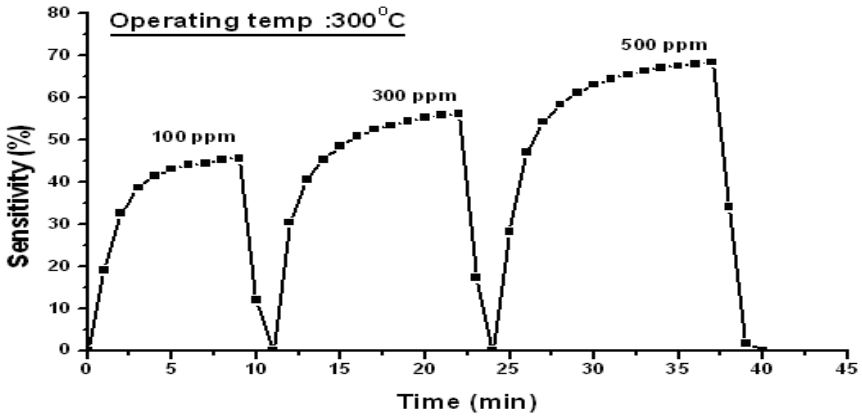


Fig.7. Transient response curves of 0. 5at% Sn-doped ZnO film for various ethanol concentrations at 300^{0}C

It is seen in the graph that the response time of the film is slightly increased due to an increase in ethanol concentration. This is attributed to an increase in the surface reaction because of a larger surface coverage of

ethanol molecules on the film surface. However the recovery time do not significantly depend on the concentration of ethanol.

4. Conclusion:

The Sn-doped zinc oxide thin films prepared by chemical spray pyrolysis technique have been studied for ethanol sensors. The optical studies show an increase in band gap due to doping, which is attributed to the Burstein-Moss(BM) effect. It is observed that compared to undoped ZnO film, Sn-doped ZnO films are highly sensitive to ethanol vapour and the magnitude of response can be varied either by changing the operating temperature or the ethanol concentration. Among the all Sn-doped ZnO films studied in this work, the 0.5 at% Sn-doped ZnO film shows the maximum sensitivity (~ 68%) at 573^0 K to 500 ppm of ethanol in air, whereas in case of undoped ZnO film, the sensitivity is found to be about 38% at the same operating temperature and concentration of ethanol in air. Further, the films show fast response and recovery at higher operating temperature.

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