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Insulating ZnO film on silicon for MIS application

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Abstract. High resistive zinc oxide thin film ($\sim 0.5\,\mu m$) was deposited on single crystal *p*-silicon (100) wafers by an inexpensive spray-CVD method and was characterized both optically and electrically. Al/ZnO/Si (MIS) device structure was subsequently fabricated and both $I-V$ and $C-V$ characteristics were studied. The semiconductor-insulator interface charge density (D_{it}) was calculated by Terman method and was found to be $3.85 \times 10^{11}\,cm^{-2}eV^{-1}$.

Keywords. Zinc oxide; thin film; spray-CVD; MIS.

1. Introduction

The change in the electrical properties of non-stoichiometric oxide semiconductors e.g. ZnO_x and TiO_x in the presence of different gases makes them useful for solid state gas sensors. Zinc oxide is a wide band gap semiconductor ($E_g = 3.2\,eV$ at room temperature) with *n*-type conductivity due to the creation of non-stoichiometry during preparation (Neumann 1981). Some reports are available on the use of ZnO for hydrogen gas sensor (Ito 1979; Saito *et al* 1985; Pizzini *et al* 1987, 1989; Sukkar *et al* 1989; Ghosh and Basu 1991). In most of the cases the change of either the resistivity or the Schottky barrier height has been utilized for gas sensing. Both single crystal ZnO wafers and spray-pyrolysed ZnO films have been used for this purpose. In the present investigation an MIS capacitor device structure has been fabricated by depositing ZnO thin film on silicon wafer by a modified and inexpensive spray-CVD method. The insulator (ZnO)-substrate (Si) interface has been characterized by $I-V$ and $C-V$ studies.

2. Experimental

2.1 *ZnO film deposition*

The spray-CVD set up was entirely fabricated in our laboratory. Figure 1(a) shows the basic design of the set-up. The spraying was done from the bottom using a spray gun containing zinc acetate solution. The silicon substrate (5×5 mm) was held from a support provided with a spring load arrangement inside a transparent quartz tube chamber. A furnace surrounded the quartz tube to maintain the desired temperature profile around the substrate. The temperature near the substrate was controlled and monitored with a chromel–alumel thermocouple. An air compressor supplied the compressed air via an airfilter-cum-regulator. With the help of a solenoid valve and a microswitch the regulated compressed air was allowed to enter the spray gun. A. R. quality zinc acetate [$Zn(CH_3COO)_2, 2H_2O$] was dissolved in deionized water and few drops of acetic acid were added to arrest its hydrolysis. This solution was used for spraying. The parameters which were optimized include substrate temperature, substrate-to-nozzle distance, single spray time and compressed air pressure. The optimum spray conditions are presented in table 1.

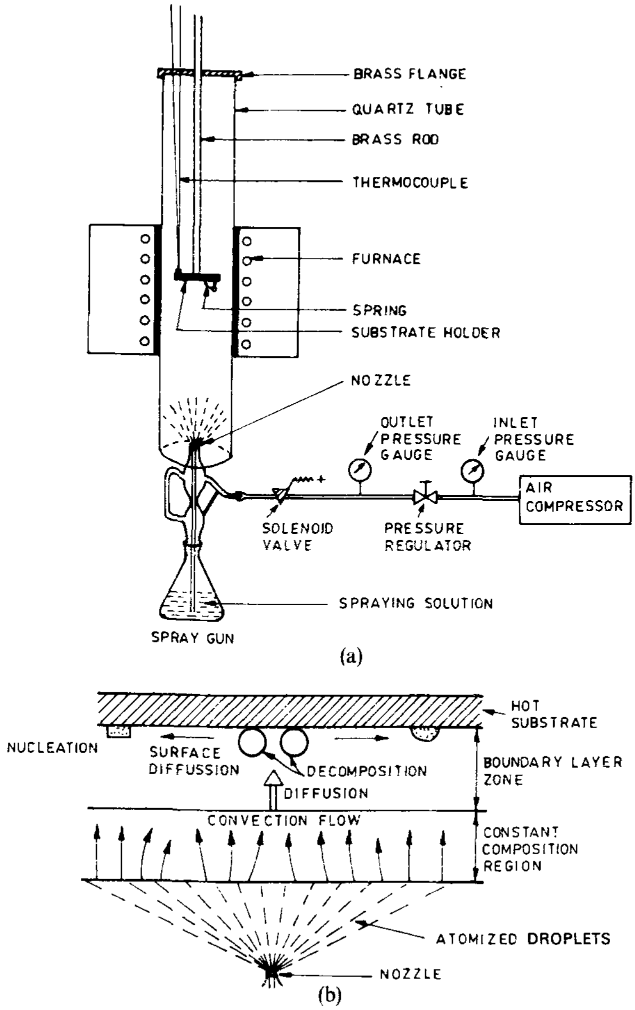

Figure 1. (**a**) Spray-CVD deposition set up and (**b**) boundary layer model.

Table 1. Optimum spray parameters for ZnO film deposition: substrate–*p*-Si(100).

Substrate to nozzle distance	10·8 cm
Substrate temperature	260°C
Single spray time	10 sec
Compressed air pressure	0·2 kg/cm^2

As shown in figure 1(b), the deposition follows the principle of boundary layer theory. A suitable temperature profile between the tip of the spray gun and the substrate was maintained. The substrate temperature was kept above the decomposition temperature of the spraying solution. The atomized droplets produced from the nozzle moved through a constant composition zone near the substrate. ZnO was deposited onto the substrate from the vapour phase and the nucleation took place via surface diffusion.

2.2 *Film characterization*

The deposited film thickness was measured using a Taylor–Hobson stylus instrument. X-ray diffraction pattern was recorded with a Philips X-ray diffractometer (PW 1729) using CuK_α radiation ($\lambda = 1{\cdot}5405$ Å). Scanning electron microscopic pictures of both unannealed and annealed films were taken using a CAMSCAN-MK II model instrument. The optical absorption spectra of the films were taken using a Shimadzu (UV 3100) spectrometer.

2.3 *MIS device fabrication and characterization*

Silicon substrates were cleaned using trichloroethylene (TCE), acetone and deionized water successively. The substrates were then etched in diluted HF solution and finally washed several times with deionized water. Subsequently the back ohmic contact was made by thermal evaporation of aluminium at a pressure of 2×10^{-5} torr and was protected against oxidation by covering with silver paste. ZnO was deposited by spray-CVD method on the front surface and the film was subsequently annealed at 500°C in oxygen atmosphere for 2 h. The thickness of the oxide film was 0·5 μm. The I–V and C–V characteristics of the MIS structure, thus fabricated, were studied. C–V was

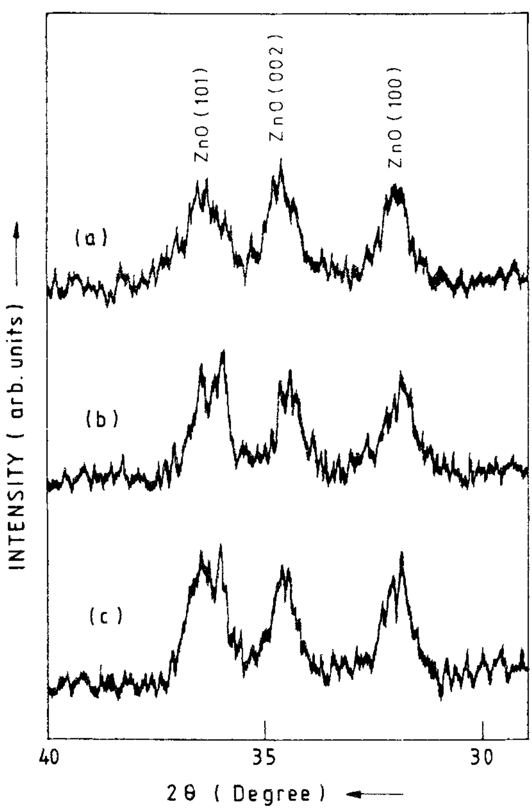

Figure 2. The X-ray diffraction pattern of ZnO on Si at room temperature. (**a**) Unannealed film, (**b**) annealed at 500°C for 2 h in O_2 atmosphere and (**c**) annealed at 500°C for 5 h in O_2 atmosphere.

measured at two different frequencies e.g. 1 MHz and 100 kHz using a Keithley 590 CV analyser. The current was measured by a Keithley 485 autoranging picoammeter and the voltage measured by a Keithley 177 microvolt DMM.

3. Results and discussion

The deposited films were found to have good adhesion to the silicon substrates. The thickness of the film was found to have an almost linear relationship with the number

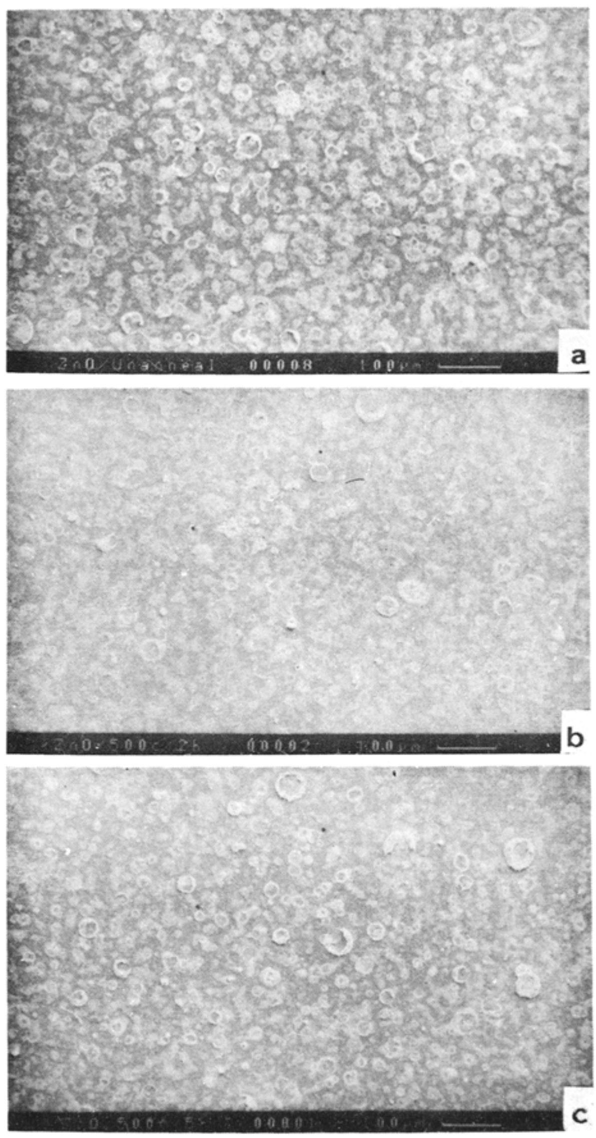

Figure 3. Scanning electron micrographs of the deposited ZnO films. (**a**) Unannealed, (**b**) annealed at 500°C in O_2 for 2 h and (**c**) annealed at 500°C in O_2 for 5 h ($\times$ 100 μm).

of sprays. X-ray diffraction study showed the formation of polycrystalline ZnO films. As shown in figure 2, the crystallinity of the as-grown film increased after it was annealed at 500°C in oxygen atmosphere. By changing the annealing time from 2 h to 5 h at the same temperature no significant X-ray peak intensity change could be observed. Surface morphology of the as-grown film and the annealed films at two different times is shown in figures 3a, b and c respectively. Non-uniformity of the film surface was found to decrease when the as-grown film was annealed. No prominent morphology change was observed with the change of annealing time from 2 h to 5 h at 500°C. From the optical absorption spectrum, the values of the absorption coefficient (α) were computed and from the plot of α^2 vs $h\nu$ a direct band gap of 3·4 eV was obtained.

I–V and *C–V* characteristics of the MIS structure were studied. By applying d.c. voltage the leakage current was measured. Figure 4 shows the *I–V* curve. From the linear region of the forward bias at 0·9 V the current was found to be 5·5 nA and using these values the resistivity of the oxide was calculated to be 2×10^{10} ohm–cm. Due to current fluctuation in the nA range more data on *I–V* could not be obtained. The *I–V* curve indicates that there is current leakage through the oxide which may be due to the presence of the mobile charge states and the gradation of non-stoichiometric composition. Figure 5 shows the *C–V* characteristics of the MIS structure. In figure 5(a) (1 MHz frequency) the three regions viz. accumulation, depletion and inversion are clearly visible. From the accumulation capacitance the dielectric constant of the oxide was calculated to be 39·5. Non-stoichiometry and microporosity of the film might be the cause of so high dielectric constant value. From $1/C^2$ vs V plot as shown in figure 6 the free carrier concentration of the substrate at the interface was $1 \times 10^{16}\,\text{cm}^{-3}$. This value is higher than the bulk carrier concentration ($4 \times 10^{15}\,\text{cm}^{-3}$) of the silicon as supplied. *C–V* characteristics show a small injection type hysteresis loop. The extent of hysteresis was judged by measuring ΔV, the difference in the value of voltage for the same capacitance. From figure 5(a), the maximum ΔV was found to be

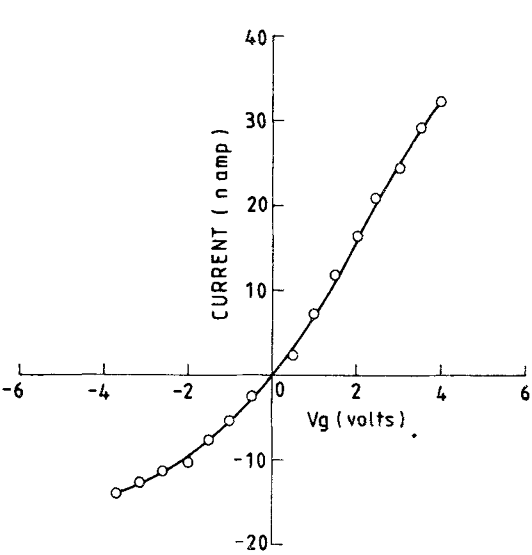

Figure 4. Current–voltage characteristics of Al/ZnO/Si (MIS) structure.

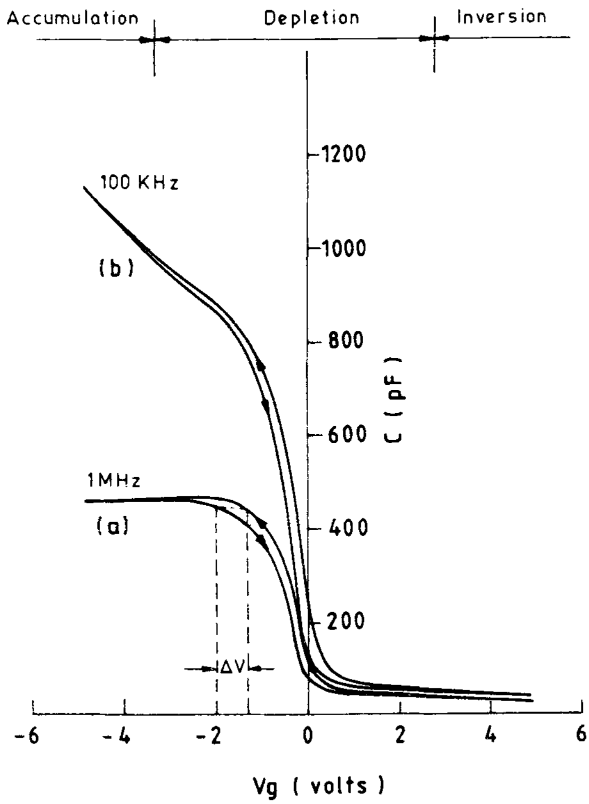

Figure 5. Capacitance–voltage characteristics of the MIS structure. (**a**) 1 MHz frequency and (**b**) 100 kHz frequency.

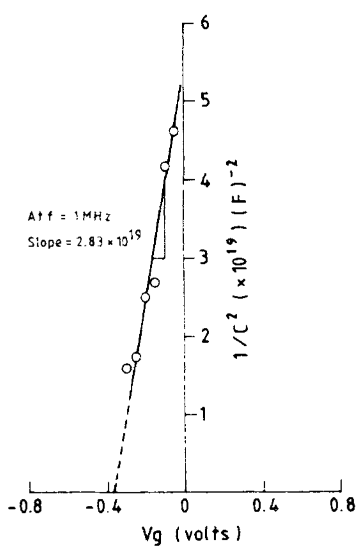

Figure 6. $1/C^2$ vs V plot at 1 MHz frequency.

0·6 V. This shows the presence of fixed oxide charge states. From the large change of capacitance value at lower frequency (figure 5(b)), it is evident that slow states are also present in the oxide film. The interface trap density (D_{it}) of the MIS structure was calculated from the $C-V$ curve at 1 MHz by Terman method (Nicollian and Brews 1982) and its value was $3{\cdot}85 \times 10^{11}\,cm^{-2}\,eV^{-1}$.

4. Conclusion

The results show that the insulating zinc oxide thin film for MIS device structures can be deposited by the simple and inexpensive spray-CVD technique. A more detailed study on the $C-V$ analysis of the MIS capacitors using this oxide and annealed under different conditions is in progress to understand the behaviour of the interface.

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