The Effect of the Oxygen Concentration on the Zinc Oxide Films Properties Deposited by Magnetron Sputtering

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Abstract
The influences of the oxygen concentration variation on the zinc oxide films structural properties were studied. ZnO films were deposited on silicon substrate by rf magnetron sputtering in reactive plasma using a zinc oxide target. They exhibited a c-axis orientation of below 0.32° FWHM of X-ray rocking curves, an extremely high resistivity of 10^{12} Ωcm and an energy gap of 3.3 eV at room temperature. It was found that a substrate temperature of 100°C, very low gas pressures of 3.35×10^{-3} Torr in argon and oxygen mixed gas atmosphere giving to ZnO thin films a good homogeneity and a high crystallinity. Measurements of the ac conductivity properties of ZnO sandwich structures with silver and platinum electrodes are reported. The frequency dependence of the both the ac conductivity and dielectric constant of thin films of ZnO have been investigated in the frequency range 5Khz-13Mhz.

It is shown that the total ac conductivity $\sigma(\omega)$; obeys the equations $\sigma(\omega) = A\omega^S$ where s is an index which increases with frequency and decreases with temperature. The dielectric constant, ε_r, lies in the range 8–9 at room temperature and is independent of the frequency in the dielectric thin films.

Keywords: ZnO; R.F sputtering magnetron; X-ray diffraction; conductivity; electrical properties; dielectric properties; optical properties.

1. Introduction

Zinc oxide is one of the most interesting II–IV compound semiconductors with a wide direct band gap of 3.3 eV [1–6]. It has been investigated extensively because of its interesting electrical, optical and piezoelectric properties making suitable for many applications such as transparent conductive films, solar cell window and MEMS waves devices [4]. The full-width at half-maximum (FWHM) of the (0 0 2) X-ray rocking curve is known to be Suppressed below about 0.5° for obtaining effective electromechanical coupling [2]. The thermal stresses were determined by using a bending-beam Thorton method [3] while thermally cycling films. ZnO has hexagonal Wurtzite structure and some properties are determined by the crystallite orientation on the substrate. For example, for piezoelectric applications, the crystallite should have the c-axis perpendicular to the substrate. According to the literature, the reactive sputtering technique has received a great interest because of its advantages for film growth, such as easy control for the preferred crystalline orientation, epitaxial growth at relatively low temperature, good interfacial adhesion to the substrate and the high packing density of the grown film. These properties are mainly caused by the kinetic energy of the clusters given by electric field [7-8] This energy enhances the surface migration effect and surface bonding state.

In previous work, we have investigated the effect of oxygen concentration on the properties of ZnO films. It has been found that the optical properties of ZnO films cannot be improved by increasing substrate temperature and the structural properties of ZnO films depend very much on the substrate temperature. Indeed, ZnO has hexagonal Wurtzite structure and some properties are determined by the crystallite orientation on the substrate. FWHM of the (002) X-ray rocking curve should be lower than 0.58 to obtain an effective electromechanical coupling [9]. In a continuation of this work the ac electrical properties of ZnO sandwich structures have been investigated as functions of both frequency and temperature.

2. Experimental

Zinc oxide films were deposited by r.f magnetron sputtering using a zinc target (99,99%) with diameter of 51 mm and 6 mm thick. Substrate is p-type silicon with (100) orientation. The substrates were thoroughly cleaned with organic.

Magnetron sputtering was carried out in oxygen and argon mixed gas atmosphere by supplying r.f power at a frequency of 13.56 MHz. The RF power was about 50 W. The flow rates of both the argon and oxygen were controlled by using flow meter (ASM, AF 2600). The sputtering pressure was maintained at $3.35.10^{-3}$ torr controlling by a Pirani gauge. Before deposition, the pressure of the sputtering system was under 4.10^{-6} torr for more than 12 h and were controlled by using an ion gauge controller (IGC – 16 F).

Thin films were deposited on silicon, substrate under conditions listed in Table 1. These deposition conditions were fixed in order to obtain the well-orientation zinc oxide films.

The presputtering occurred for 30 min to clean the target surface. Deposition rates covered the range from 0.35 to 0.53 μm/h. All films were annealed in helium ambient at 650°C for 15 mn. After deposition, silver dot electrodes were evaporated on the sample ZnO/Pt/Ti/Si using an electron gun evaporation system, in order to make a metal–oxide– metal structure useful for electrical measurements. These were carried out in a vacuum chamber evacuated to approximately 10^{-3}Torr. Both the electrical conductivity and dielectric constant were measured as a function of temperature (30–250°C) and frequency (5 Hz–13 MHz by a capacitance bridge technique), with a Hewlett-Packard LF impedance analyzer 4192 A between the silver dots and Pt electrode bottom. Temperature was measured with a Doric thermometer (Trendicator 400K/8C), and a high frequency probe station with a network analyzer (HP8753ES) were used to measure the resonant frequencies of the fabricated device

3. Results and discussions

3.1 Effect of the oxygen concentration

Figure 1 show the XRD pattern for samples deposited at several oxygen concentrations (ranging from 10% to 30%). The peak at about 34° corresponds to the diffraction from the (0 0 2) plane of the ZnO [10]. No other peak could exhibit preferred c-axis orientation. The intensity of the (0 0 2) peak increased as the oxygen concentration is increased to 20% due to the improvement of the films crystallinity. The presence of (0 0 2) peak indicates that the films have a strong c-axis orientation perpendicular to the surface at the substrate. However, at 30%, the (0 0 2) peak intensity is decreased which indicates that the degree of crystallinity of the films is deteriorated. Such deterioration in the degree of crystallinity with the oxygen concentration was also observed by Kim et al. [11] in RF magnetron sputtered films. Again a preferred orientation along the (0 0 2) crystal plane at 100% in beam deposition [12] where as in RF sputtered it was noticed that the films formed at 50% exhibited a single phase of ZnO with (0 0 2) orientation [13]. The variation in the results may be due to differences in the deposition methods where to difference or the target used.

Looking at the evolution of the peak intensity as a function of oxygen in Figure 2 rate, we can conclude that the best crystal orientation is obtained for an oxygen level of 20% in the gas mixture Ar / O_2 and the experimental conditions listed in Table III.6. From these results, we can say that our zinc oxide samples crystallize better low oxygen levels, and in particular for an oxygen level of 20%. This dependence on the crystal orientation of ZnO thin films with the oxygen in the gas mixture Ar-O_2 rate was studied in prior work.

It has been shown that the crystal orientation in the (002) plane along the c axis perpendicular to the substrate surface is obtained at oxygen levels of 15-40% [14-16] by sputtering a metal target pure zinc. This confirms our results.

To observe the surface and the portion of our deposits ZnO obtained by varying the oxygen concentration in the gas mixture, we used scanning electron microscopy (SEM).

This characterization technique provides information on the morphology of the layers (dense or sparse) and the structure (columnar or not look).

The photographs obtained are shown in Figure 3. They represent the views of surfaces and also slices. This tells us about the thickness of thin films. We note that the layers are dense, no visible holes. The surfaces show no significant irregularities. In addition, the layers prepared at 20 and 30% have a pretty sweet relief surface. Despite the density of the layers, we observe the appearance of columnar layers is a conventional structure of ZnO thin films [17,18]. This is because the grains are tight to each other. Also, with the low power injected into the discharge, the change in temperature of the substrate, after deposition, is very low, minimizing the effect of impacts, resulting in fewer holes and higher densification in relation to the model M-D Chart area [19].

Indeed, the surface of our films is comparable to the surface of the transitional structure (area called T diagram area) that defines the boundary of zone 1, when the T/T_m ratio is substantially equal to zero on substrates ideals (a perfectly flat and zero roughness). As the ratio T/T_m is 0.055, we have a structure with one small area difficult to differentiate fibrous appearance of crystal grains with dense enough to give the layer suitable mechanical properties.

3.2 Transmittance and band gap

The effect of oxygen on the transmission of ZnO thin films is shown in Figure 4. A decrease in the transmission measurement is observed that the percentage of oxygen in the gas mixture (Ar - O_2) increases in the region of low wavelength. Is the maximum observed for the transmission of oxygen equal to 20% and the minimum

transmission are higher. In addition, the difference between the transmission extrema (Tmax - Tmin) is larger for this sample. This reflects a higher refractive index.
To highlight these observations, we have shown in Figure 5 changes in the refractive index as a function of oxygen concentration in the gas mixture at a given wavelength (λ = 600 nm). We find that the influence of the gas mixture on the refractive index is significant only when we have an oxygen level of 20%. In addition, we note a decrease in the index with the increase of oxygen in the gas mixture. We can attribute this phenomenon in comparison with X-rays, the crystallographic structure of disorientation. Indeed, the structural study showed that the optimum oxygen level, to develop highly crystalline ZnO layers was 20%.

3.3 A.C. measurements

Figure 6 shows the variation of conductivity as a function of the frequency at room temperature. We note that the conductivity exhibits the same behavior. The frequency dependence of the conductivity is linear.
The ac conductivity changes with the oxygen in the gas mixture. At room temperature, the conductivity decreases with the oxygen to reach a minimum value of 20%, and then increases as the oxygen in the gas mixture rate increases. This result is in agreement with the literature. Indeed, it has been reported that the development of ZnO films by magnetron sputtering are used to obtain a very low ac conductivity for oxygen content between 20 and 25% [13,20].
A likely explanation for the dependence of oxygen in the gas mixture of the ac conductivity is the following: increasing the oxygen product defects responsible for ion conduction rate, resulting in poor crystallization of the layer. Indeed, on both sides of 20% oxygen, the increase in conductivity can be explained by the formation of certain types of aggregates (due to complex interactions between the oxygen cathode gaps and defects) in the crystal structure.
We studied the influence of oxygen in the gas mixture on the dielectric constant. The results obtained are shown in Figure 7. It shows the influence of oxygen content on the dielectric constant. For this study it appears that increasing the oxygen content in the gas mixture up to 20% of O_2 causes a decrease in the dielectric constant to reach the minimum value 8.4. Beyond this rate, the dielectric constant increases. This behavior could be explained in part by changes in the grain size of ZnO. Indeed, a significant change in grain size means a breakdown of the layer. Because beyond 20%, the increase of the dielectric constant can be attributed to a rearrangement in the atomic structure. This can significantly reduce the elementary dipoles.
These results confirm the observed behavior of the change in conductivity as a function of frequency. Indeed, the values of the dielectric constant observed at 20% are substantially identical. They are very close to the value of the dielectric constant of solid zinc oxide which is equal to 8.5 [21].

4. Conclusion

In conclusion, the best quality ZnO films in terms of crystalline structure have been grown on silicon substrate at oxygen concentration at 20% employing RF magnetron sputtering method from a metallic zinc target. XRD shows that the films are well oriented where the c-axis grows normal to the substrate plane. The zinc oxide thin films grew preferentially along the [0 0 1] direction. All the ZnO thin films deposited by RF magnetron sputtering have compressive stress. The crystallographic characteristics correlated with a direct band gap of 3.3 eV and a high resistivity of 1012Ocm. Consequently, well-oriented zinc oxide thin films with both structural properties and high optical transparency could be successfully deposited by RF magnetron sputtering.
For the oxygen concentration at 20%, we obtain a 10 KHz, a dielectric constant of 8.4 at room temperature. The dielectric constant is strongly influenced by the deposition parameters. By linking the variation of the dielectric constant as a function of oxygen concentration in the gas mixture to the evolution of the grain size of ZnO layers developed, we conclude that the structure of the material plays an important role in the dielectric behavior.

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Table 1:. ZnO sputtering conditions

Samples	Rate O_2%	Time filing (minutes)	Pression (mTorr)	RF Power (W)	Target to substrate distance (cm)	Substrate temperature (° C)	Thickness (µm)
ZnC1	10	150	3,35	50	7	100	5
ZnC2	20						2,75
ZnC3	30						2

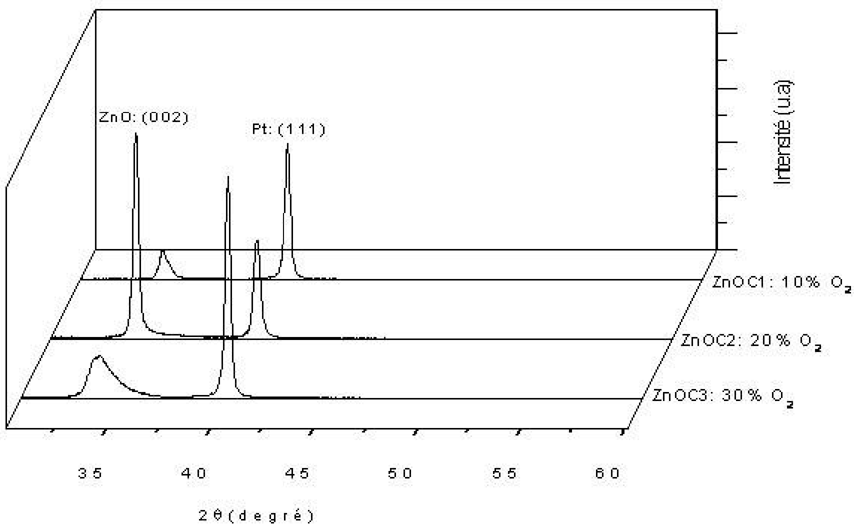


Figure 1: Variation of XRD diagram from ZnO films as a function of the ratio gas mixture A_r/O_2.

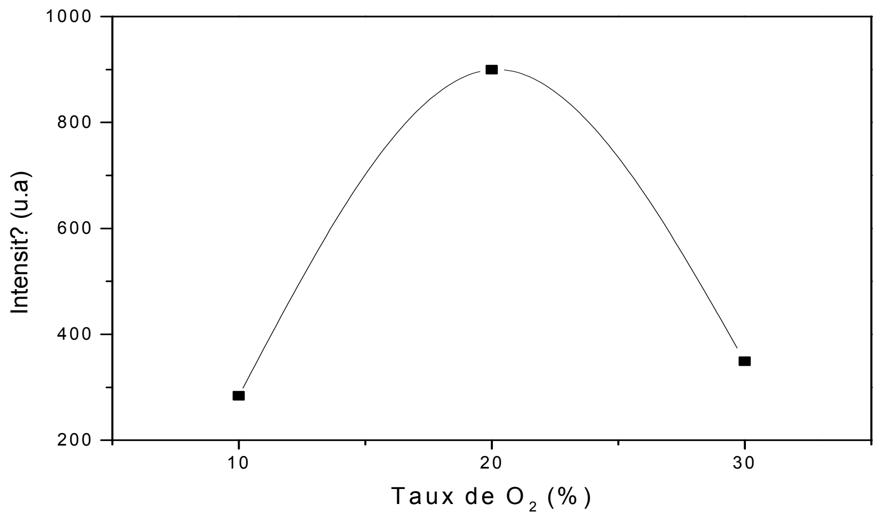
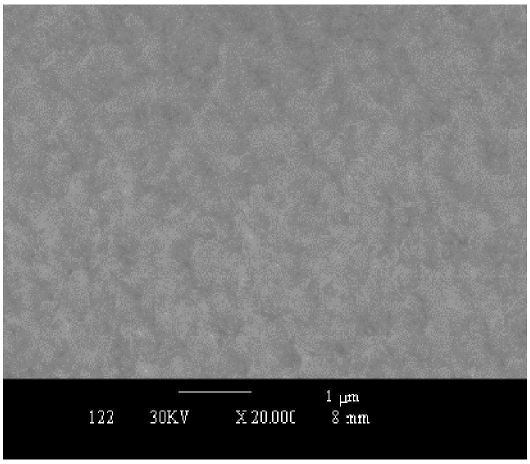
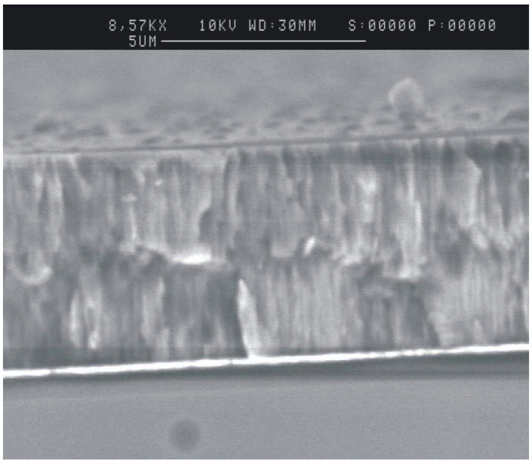
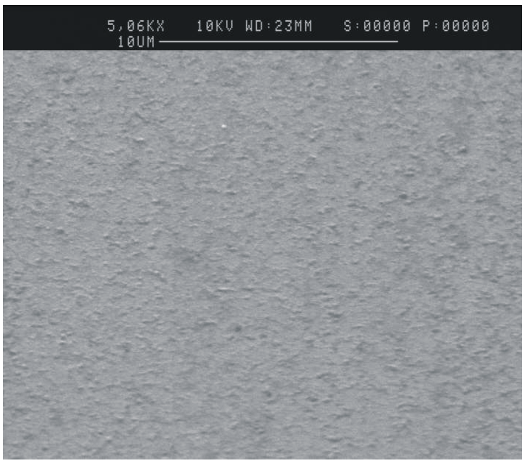


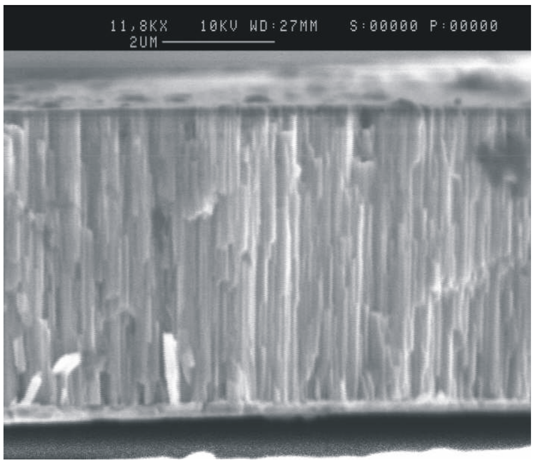
Figure 2: Change in intensity of the diffraction peak as a function of oxygen concentration



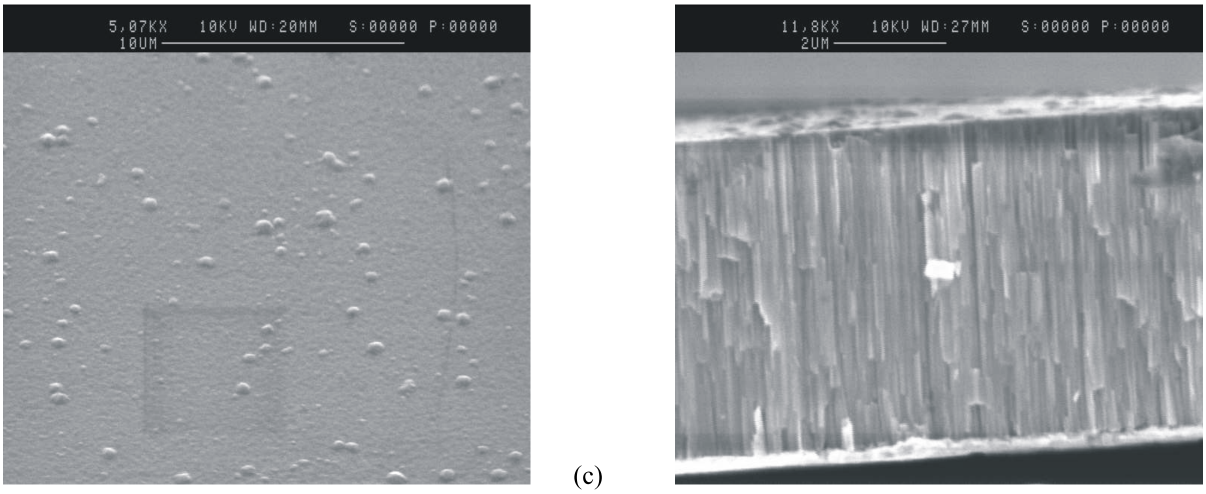


(a)





(b)



(c)

Figure 3: M.B.E image of ZnO deposited at (a) O_2 = 10%, (a) O_2 = 20% and (a) O_2 = 30%.

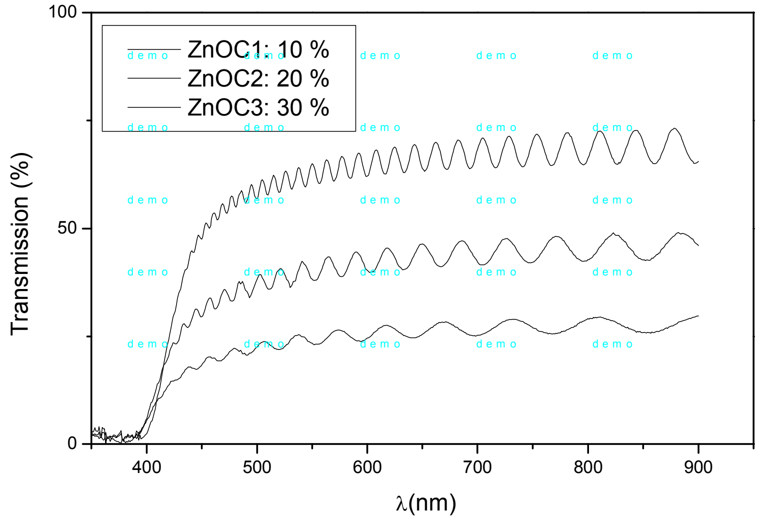


Figure 4: Transmission spectra of ZnO films on the oxygen concentration.

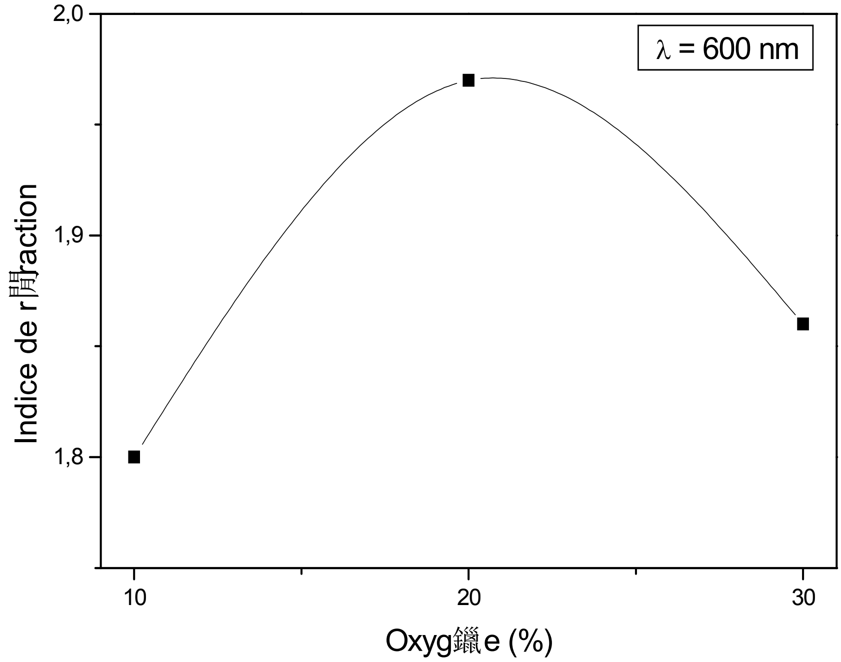


Figure 5: Variation in refractive index as a function of the oxygen rate constant λ.

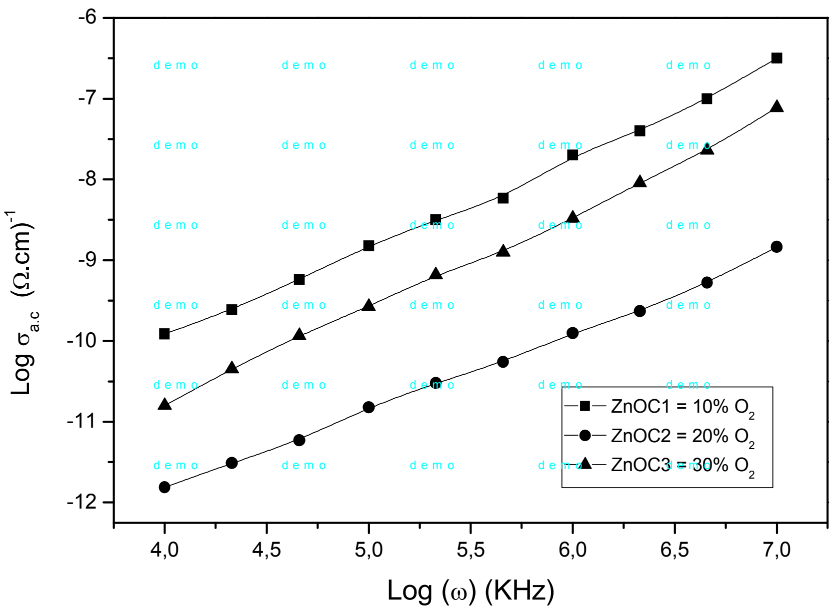


Figure 6: Frequency dependence of the oxygen concentration.

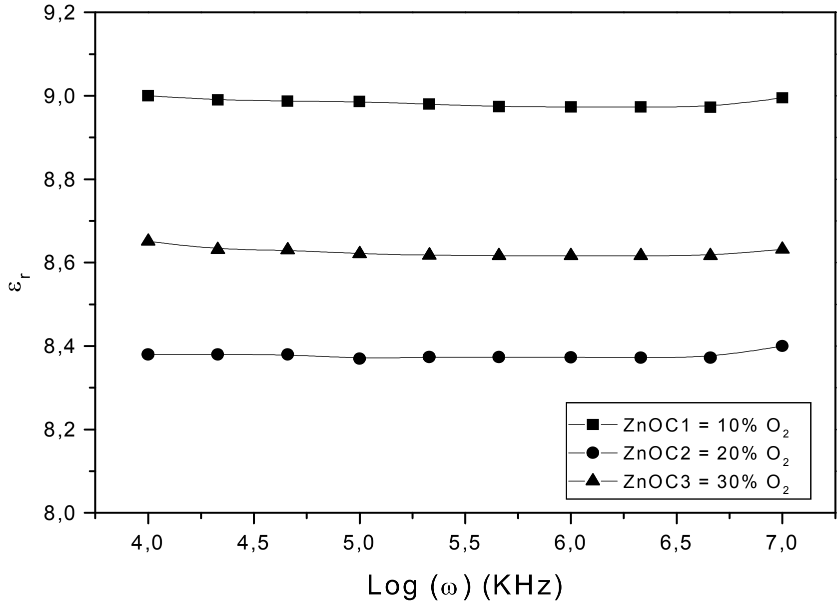


Figure 7: frequency dependence of ε_r at different oxygen concentration.