

## INELASTIC ELECTRON TUNNELING SPECTROSCOPY FOR Zn-ZnO-Pb TUNNEL JUNCTIONS

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### Abstract:

*Inelastic Electron Tunneling Spectroscopy (IETS) technique is applied to Zn-ZnO Pb tunnel junctions to probe the vibrational structure of minute organic molecules doped on the oxide layer. Spectrums are obtained for methanol, benzoic and acetic acids. The spectrums reveals the direct mechanism involved between the dopants and the oxide layer.*

### Introduction

While investigating band structure effects using Al-Al<sub>2</sub>O<sub>3</sub>-Pb tunnel junctions, Jaklevic and Lambe (1) decided to plot the second derivative ( $d^2I/dV^2$ ) versus applied voltage  $V$ . To their surprise they found that the plots resembles those obtained by infrared spectroscopy techniques for molecular vibrational spectrums. To solidify their findings they doped the oxide layer with minute organic molecules. The results showed a spectrum containing peaks at the expected positions for vibrational modes. Their discovery layed the foundation for a new spectroscopy technique, known today as Inelastic Electron Tunneling Spectroscopy (IETS). In this paper we will investigate the effects of three dopant materials, methanol, benzoic and acetic acids on zinc oxide barriers.

### Sample Preparation

The evaporation of the two metal electrodes was accomplished using an ordinary but high quality vacuum system. We found that prior to the evaporation of the zinc base electrode, that it is best to chill the substrate at liquid nitrogen temperature. This resulted in a higher sticking coefficient between the zinc electrode and the substrate. The zinc strip had a mirror like appearance with dimensions 2 cm long by 2 mm wide and a thickness of 2000 Å. Oxidation of the zinc strip was accomplished by exposing the samples to atmospheric pressure for about one week. Application of the dopant material was simply done by either exposing the oxide to its vapor form (acetic acid), or applying few drops of the diluted solution (methanol and benzoic acid). Finally the cross-wise lead strip was similarly evaporated.

### Experimental Set-Up

Fig. (1) shows the experimental block diagram. A dc bias voltage and an rf current, whose amplitude  $\mathcal{E}$  is  $0.3 \leq \mathcal{E} \leq 1.4$  mV and frequency is 500 Hz, are driven through the tunnel junction. The rf current is swept by a saw tooth voltage of frequency 100 Hz. The current developed across the junction is given by (2);

$$I(V) = I(V_0) + (dI/dV) \bigg|_{V_0} \int_0^{\mathcal{E}} \cos(\omega t) + (d^2I/dV^2) + \frac{d^3I}{dV^3} \bigg|_{V_0} \int_0^{\mathcal{E}} (1 + \cos(\omega t)) \sin \alpha + \dots$$

where  $I(V_0)$  is the dc bias. To simplify tuning arrangements, the lock-in amplifier is maintained at 1000 Hz and the modulation frequency is only changed. It is 500 Hz for the second derivative measurements (spectrum measurements), and 1000 Hz for first derivative (conductance) measurements. Finally the sample is mounted on a special probe and directly immersed in liquid helium.

### Results and Discussion

The oxide layers investigated had an average thickness of 26 Å and resistance of 30 ohms (3). Fig. (2) shows the spectrums obtained for the three dopants. In all three spectrums, the ZnO phonon spectrum reveals a strong peak around the 73 mV mark. This peak is the hall mark of the ZnO phonon spectrum and must always be present. Other fundamental ZnO phonon frequency peaks are observed near 43, 50, and 58 mV, (Fig. (2-a)), and near 45 and 55 mV, (Fig. (2-b)), and around 42 mV, (Fig. (2-c)). Multiple ZnO phonon frequencies are detected near 128 and 141 mV, (Fig. (2-a)), and near 121, 131, and 138 mV, (Fig. (2-b)), and 142 mV, (Fig. (2-c)) (4). For undoped tunnel junctions, the ZnO phonon spectrum is similar to that of Fig. 2-c for the range  $0 \leq mV \leq 150$ . On comparing spectrum to those of figure 2-a and 2-b we see that the last two spectrums are better resolved and higher in intensity. Now since all samples were similarly prepared and oxidized, then such difference must only be related to the dopant. The effect of the dopant on this behavior will be understood after discussing the dopant spectrum.

Fig. 2-a shows the spectrum obtained for ZnO doped with acetic acid. The spectrum exhibits a strong structure around 344 mV attributed to a Zn-H band (5). Two other peaks are also detected near 171 and 437 representing a Zn-C band (5). For the methanol spectrum, Fig. 2-b, the peaks near 171, 182, and 211 mV represents a Zn-C band and a Zn-H stretching mode (5). In Fig. 2-c, benzoic spectrum, the peak at 358 mV is a C-H stretching mode. The structure within the range 230 mV - 300 is probably due to C-O stretching modes (5). In all three spectrums there is a structure around the 100 mV mark, which is due to air oxidation and represents a C-H rocking mode (6). From Fig. 2-c we can deduce three features that indicate that benzoic acid did not react chemically with the oxide layer, but was rather adsorbed on it. First, the ZnO phonon spectrum has not changed. Second, there are no peaks (in the dopant spectrum) that contain zinc atoms. The third

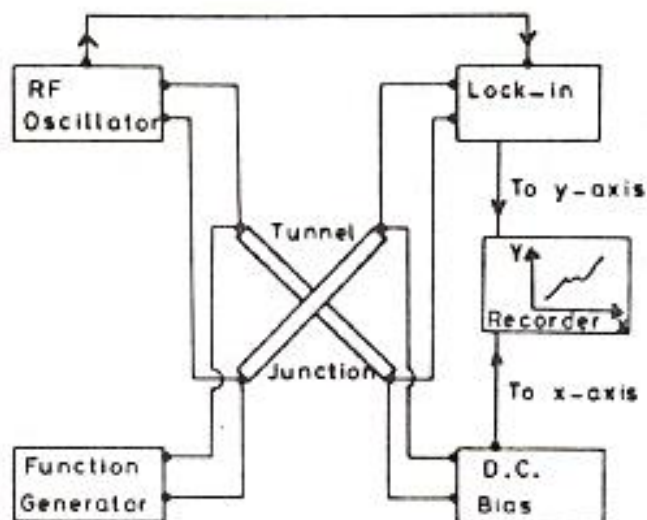


FIG. 1. Circuit Block Diagram

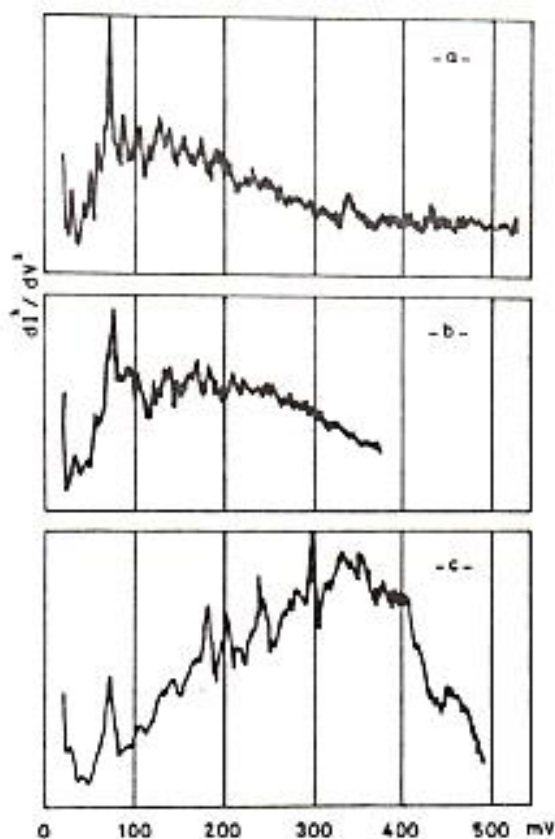


FIG. 2. 2-a: Acetic Acid Spectrum  
 2-b: Methanol Spectrum  
 2-c: Benzoic Acid Spectrum

and last is that the dopant spectrum is well resolved and high in intensity. This last feature indicates that benzoic molecules did not penetrate into the oxide layer but rather resided on the surface. This conclusion is supported by the orientational selection rule that states that molecules situated close to the surface will have a vibrating mode perpendicular to the surface resulting in peaks that are well resolved and high in intensity. Such selection rule does not hold for molecules residing deep in the oxide (7). On the other hand, in Fig. 2-a, there are peaks that contain zinc atoms, an indication that acetic acid reacted chemically with the oxide to give us a new product which is zinc acetate salt. The reaction did not cover the complete oxide layer, other wise no ZnO phonon peaks would be detected. Hence in this case the insulating barrier can now be viewed as a double barrier of which the original thickness is the same. The first layer is ZnO layer, and the second is the salt layer. Now from tunneling measurements it is known that as the insulating barrier becomes thinner, the spectrum peaks become more sharper. Thus on comparing the ZnO phonon spectrum to that of the salt spectrum, we see that the ZnO phonon peaks are better resolved and higher in intensity. This means that the ZnO layer is much thinner than that of the salt. By the same token, the methanol spectrum can also be explained. Finally in all three spectrums the background signal increases (an increase in conductivity) then it declines. The signal decline is an indication that the junction can no longer support higher currents. Such behavior is a function of the junction thickness, since the thicker the junction, the higher its resistance, the higher the maximum current it can handle. Thus on comparing all spectrums together, we see that the turning points is further out for the benzoic spectrum. This is also an indication that the ZnO layer for this spectrum is thicker than that for methanol and acetic acid. This result then also supports our ideas mentioned above about the mechanism of reaction between the dopants and oxide layer.

### Conclusion

IETS technique has been applied to Zn-ZnO-Pb tunnel junctions doped with methanol, acetic and benzoic acids. The spectrums not only reveal the vibrational modes, but also gives us a direct determination of the type of reaction mechanism involved between the dopant and oxide surface. Such technique holds great promises for surface studies, physical and chemical, and also for heterogenous catalysis applications especially when low temperature environments are required.

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