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Observation of localized states in barrier regions of metal-insulator-metal tunnel junctions*

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Small oscillatory structure in the tunnel conductance of Mg-insulator-metal junctions at very low temperatures is reported. Data on the effect of external influences such as thermal, voltage, and current annealing as well as application of a magnetic field are presented. The possibility that the structure may be due to resonant tunneling is discussed.

INTRODUCTION

In this paper, we report the observation of oscillations in tunnel conductance of metal-insulator-metal junctions. These oscillations are believed to be caused by localized impurity states in the insulating barrier or at the barrier metal interface.

The oscillations were first observed in the course of a detailed investigation of nonequilibrium effects in tunneling. It is known that the high-resolution conductance curves of a nonmagnetic, normal metal-insulator-metal junctions at low temperatures exhibit a conductance dip similar to that shown in Fig. 1 commonly referred to as zero bias anomaly (ZBA). This ZBA is due to an electron bottleneck caused by the nonzero relaxation time of tunneling electrons.[1] In some junctions we found superposed on this ZBA a series of oscillations similar to those in Fig. 2. These oscillations form the content of this paper.

The first observation of these oscillations occurred in Mg-Pb junctions. Unfortunately, the low-energy structure in such junctions is very near to the strong background associated with both the superconductivity of the Pb electrode and the appearance of inelastic phonon-assisted tunneling.[2,3]

In view of this we have decided to investigate the oscillations in Mg-Au junctions, because the large ionic radius of the counter electrode (Au) makes junction preparation relatively easy. In general, it is more difficult to prepare good tunnel junctions with counter electrodes of small ionic radii since these penetrate deep into the barrier layer.[4] However, oscillations in other type of junctions (Mg-Mg, Mg-Bi, Mg-Pb) were observed. The detection of phonon emission in Mg electrode indicated that the measured current was due to tunneling.

EXPERIMENTAL

The junction preparation was carried out in a vacuum system with a liquid-nitrogen trap installed between the vacuum chamber and the diffusion pump. This arrangement reduces the contamination of the insulating layer by hydrocarbons. A glow discharge technique of barrier formation was used to prepare tunnel barriers on Mg. The Mg was oxidized in pure O_2 at pressures 100–200 Torr. The glow discharge was maintained for 1–3 min during oxidation. The similar technique was used to prepare junctions of Mg in a nitrogen environment. In this case the discharge was kept for 40–80 min and pressures between 400 and 600 Torr. It has been shown[5] that Mg heated in a nitrogen environment containing traces of water vapor and oxygen reacts preferably with these thus inhibiting the formation of nitride. Such junctions, therefore, probably also have had MgO barriers.

Some junctions were purposely doped with hydrocarbons during formation of the barrier layer. This was achieved by passing oxygen (nitrogen) gas through a flask containing light machine oil heated close to its boiling point. The verification of oil absorption was performed by observation of inelastic spectrum of the junction in the bias range where the hydrocarbon peaks were located.[3,4] These junctions showed no oscillatory effects at all.

The measurements were carried out by a combination of bridge techniques and harmonic detection described earlier.[6]

OBSERVATIONS

Oscillations were observed in a variety of tunnel junctions having zero bias resistances (at He temperatures) between 15 and 8000 Ω and film thicknesses of 600–30 000 Å. The observed oscillations were usually located within ± 25 meV of the zero bias. A typical junction is shown in Fig. 3. Oscillations persist to 10 meV and attenuate beyond this bias. Figure 4 shows the conductance curb in a greater detail in ± 5-meV region. It can be seen that the oscillations are much more pronounced at 1 K than at 4 K. Similar results are shown in Fig. 5.

It was found that these oscillations could be significantly perturbed in three ways. The first of these consisted of allowing the junctions to warm

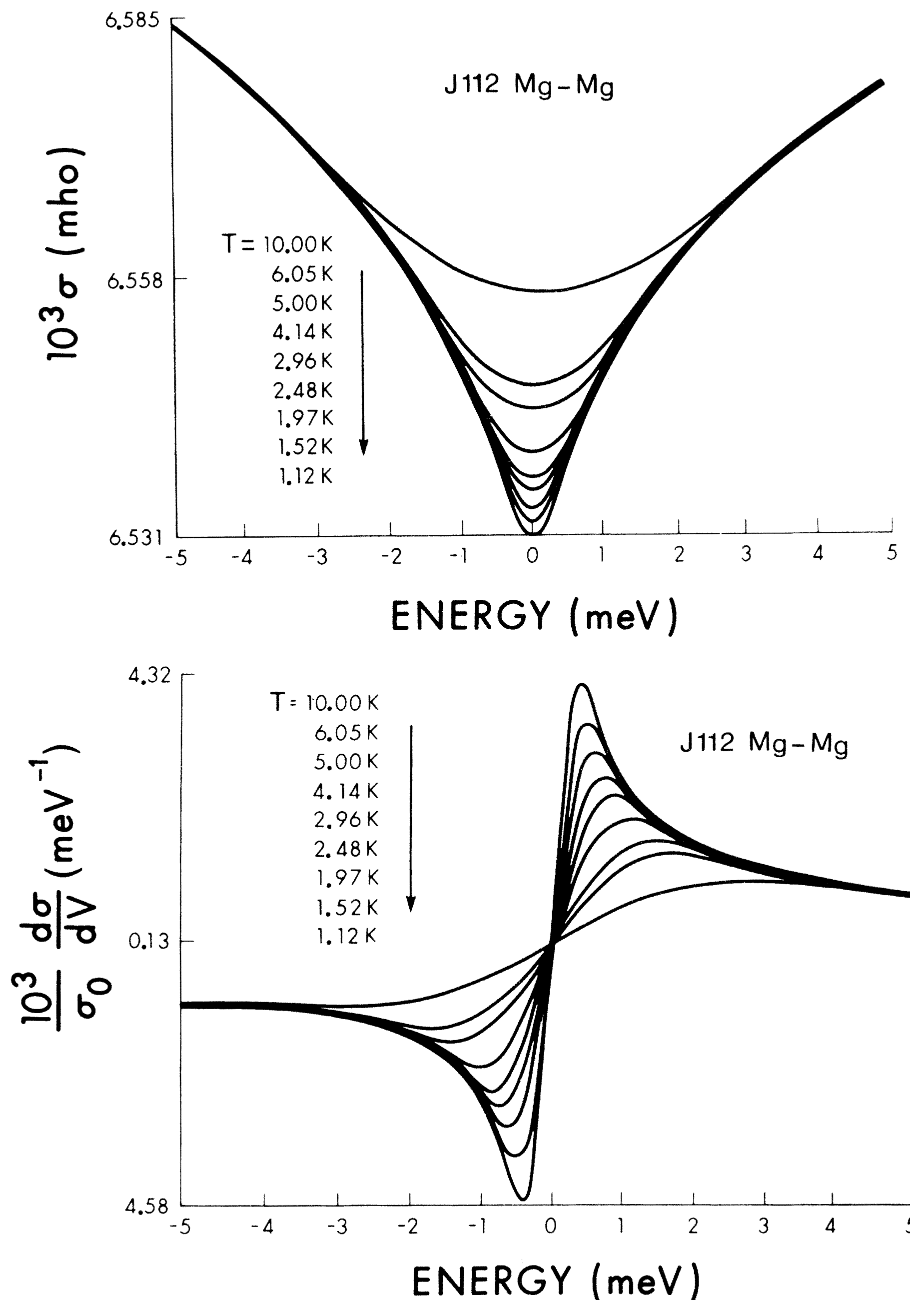

FIG. 1. Typical zero bias anomaly (ZBA).

up to room temperatures in a vacuum for a day or two and subsequently repeating the measurements at He temperatures. This method will be called thermal annealing. The second method consisted of applying biases up to 1 V across the junction for periods up to 1 h at He temperatures. We refer to this procedure as voltage annealing. Finally, passing a dc current up to 0.5 Å through either film at He temperatures, we refer to this as current annealing.

Prior to thermal annealing junction 080*B*, Fig. 6, after initial cool down had oscillations in its characteristics. Thermal annealing resulted in a 36% decrease in zero bias resistance, while the resistance change from zero bias to 5 meV remained approximately constant and about 2%. The magnitude of oscillations in this junction was so greatly reduced by annealing that they were no longer observable with the *same gain* employed earlier.

A typical result of voltage annealing is shown in Fig. 7 and was the result of an application of 0.7

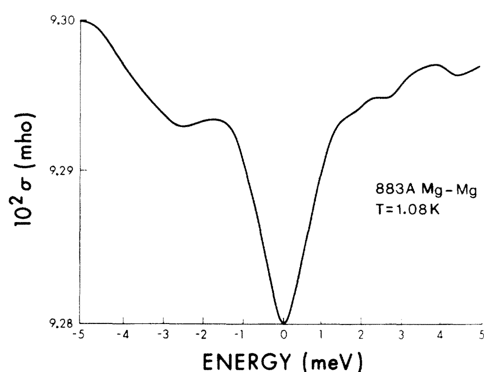

FIG. 2. Mg-Mg junction showing oscillations superposed on the ZBA.

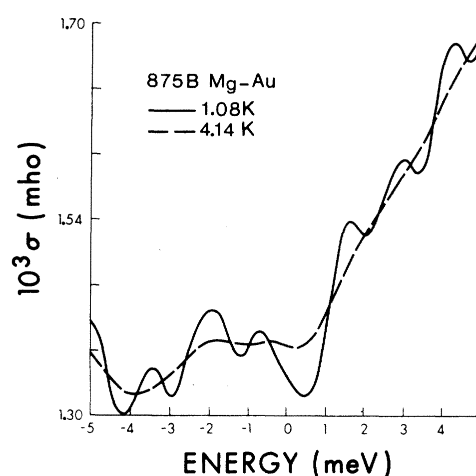

FIG. 4. Oscillations in the ±5-meV region for two different temperatures.

V (Mg positive) across the junction at He temperatures for 1 h. Current annealing gives results similar to those shown in Figs. 6 and 7.

Defining $\sigma_4(0)$ and $\sigma_1(0)$ as the zero bias conductivities at 4 and 1 K, respectively, the ratio

$$[\sigma_4(0) - \sigma_1(0)]/\sigma_1(0)$$

remained constant (less than 2% change), regardless of the method of annealing. Since this zero bias structure arises from deblocking of electron states in the vicinity of the Fermi energy, we conclude that boundary and impurity scattering mechanisms which tend to unblock the tunneling states in the metal electrodes are unaffected by the annealing process. Thus only a change in the electron transition rate is responsible for changes in junction resistance upon annealing.

It should be noted that no oscillatory structure was ever observed in junctions in which hydrocarbons were purposely adsorbed during barrier preparation.

DISCUSSION

It seems reasonable to assume that the oscillations (periodicity of 0.8–2.7 meV) are due to resonances associated with a presence of discrete channels for tunneling electrons which open up at definite values of the applied voltage.

Box quantization[7] (standing waves) can be ruled out as no correlation between the film thickness and periodicity of oscillations was seen. If our observations were due to box quantization then film thicknesses of 25 000–30 000 Å are required to obtain oscillations with periodicity of about 1 meV.

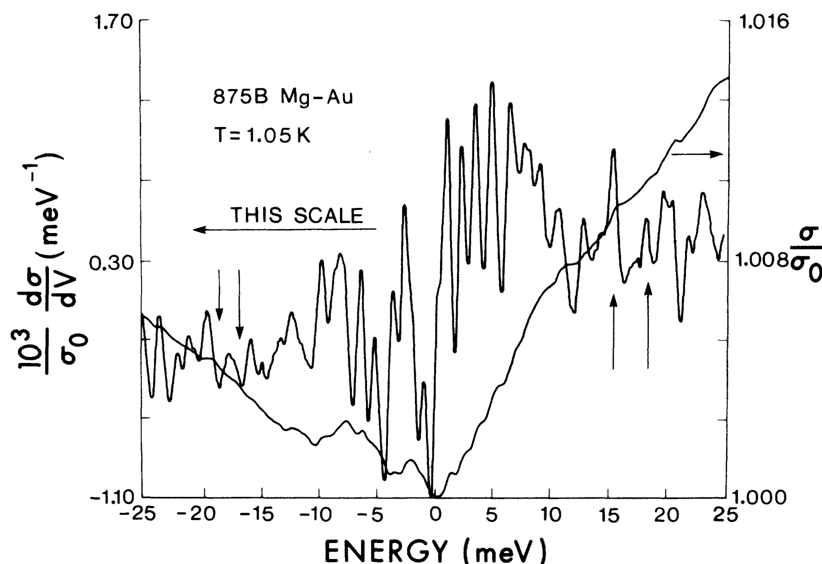

FIG. 3. Oscillations in the tunnel conductance of a Mg-Au junctions. The arrows show the location of magnesium phonons. The thickness of Mg film was 740 Å, while that of Au was 650 Å.

This thickness range is well above the thickness of either Mg or Au films for junctions shown in Figs. 4 and 5. Our room-temperature evaporated films would surely lack the smoothness required to reproduce the beautiful data of Jacklevic *et al.*[7]

As mentioned in the previous section the character of the oscillatory pattern could be modified by either voltage, current, or thermal annealing, the new character remaining invariant in the absence of further annealing. Since annealing does not affect the ZBA, which depends primarily on relaxation time within the metal electrodes themselves, we must conclude that the annealing effects occur either within the barrier or at barrier electrode interface. Simple barrier growth[8] (changes in the thickness and height of the barrier) would affect only the structureless background[9] of the junction conductance and are of no interest to us here. Inelastic tunneling effects can be similarly excluded since energies at which such processes take place are certainly independent of any annealing effect.[4]

The presence of an impurity inside the tunneling layer, on the other hand, could result in a resonant two-step tunneling process. This is possible if the impurity within the barrier has an attractive potential having bound states.[10–12] Under favorable conditions a new tunneling channel can open up in which the electron goes from the metal to the adsorbed impurity, where it is partially localized, and then continues through a reduced

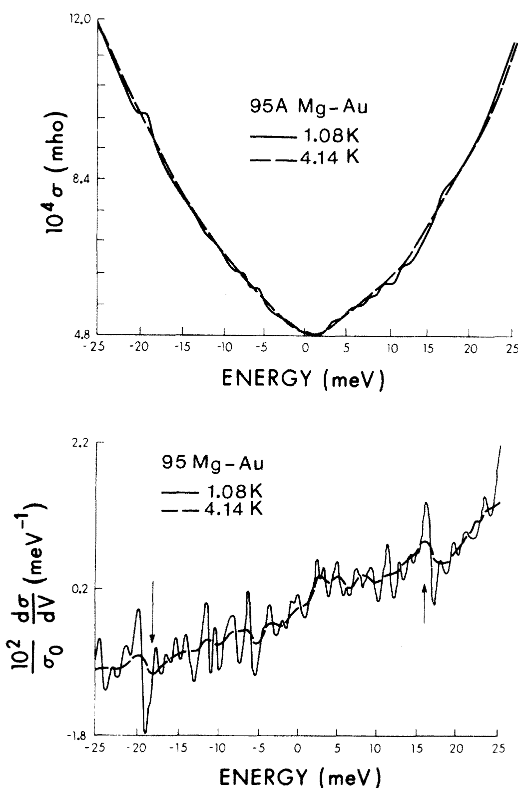

FIG. 5. Oscillations in the ±25-meV region at two different temperatures. The arrows show the longitudinal phonon peaks in Mg. This junction was prepared in a nitrogen environment. The Mg and Au films were 1500 and 800 Å thick, respectively.

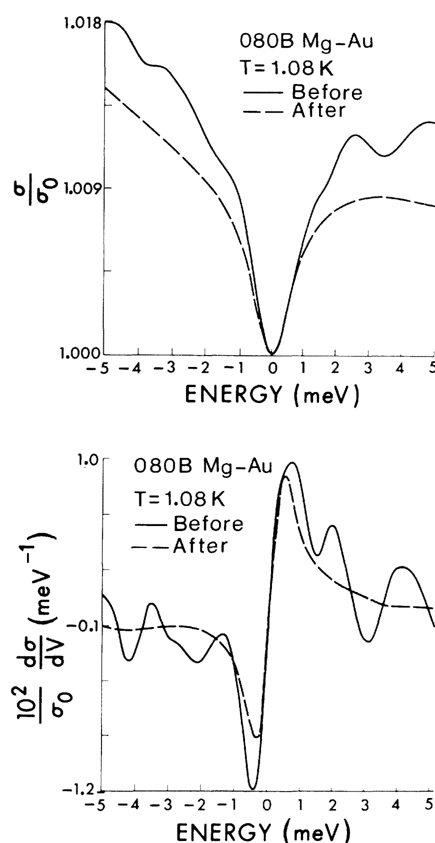

FIG. 6. Typical junction in its virgin state (solid line) and after thermal annealing (dashed line). (Mg—18 000 Å, Au—1000 Å.)

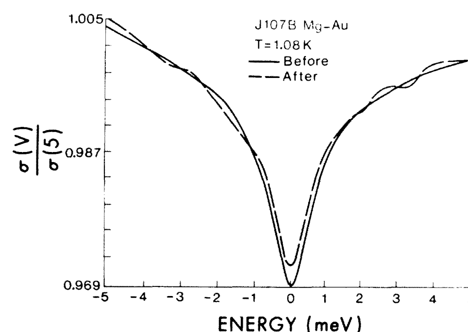

FIG. 7. Typical junction in its virgin state (solid line) and after a voltage anneal of 0.7 V for 1 h at He temperatures. (Mg—10 300 Å, Au—1500 Å.)

barrier into the second electrode. The degree of electron localization is very important in distinguishing between two possible processes. An impurity state with a deep and narrow attractive potential can lead to a capture of the tunneling electron with characteristic lifetime longer than the barrier tunneling time. The subsequent decay of the bound state with the transmission of the electron into the second electrode is essentially equivalent to Giaever-Zeller[10] tunneling. A uniform distribution of bound-state energies then leads to a large temperature-dependent decrease in conductance. In contrast, the effect of the impurity potential on the tunneling electron can be such as to allow only for a resonant buildup of the electron wave function in the potential well with localization times shorter than the tunneling times. This will lead to an increase in the electron probability amplitude inside the forbidden region, resulting in an enhanced transmission coefficient. We believe that this type of resonant transmission is responsible for the structure seen in our tunneling characteristics.

Schmidlin[13] analyzed the effect of impurities on the barrier profile and found that throughout the low-voltage region a positive ion substantially reduces the barrier height in its locality. The local decrease of barrier height around the impurity can then be instrumental in establishing resonant transmission via intermediate energy levels existing inside the barrier.

A simple one-dimensional treatment of a tunneling process in which the insulating layer contains an impurity with a resonance at $E_R = eV_R$ shows[11] that resonant tunneling takes place above a voltage V,

$$V = |V_R| + xV/t,$$

where x is the position of the impurity inside the barrier of thickness t. This resonant tunneling manifests itself by a steplike increase in tunnel conductance. A more detailed[14,15] three-dimensional investigation shows that such a resonance will have a Lorentizian shape resulting in an enhancement of the transmission probability by a factor of

$$\Gamma^2 |T_{\text{imp}}|^2 / [(E - E_R)^2 + \Gamma^2],$$

where Γ is the width of the level and $|T_{\text{imp}}|$ gives the opacity of the barrier in the presence of an impurity.

This type of calculation can be extended to several impurity levels having different resonant energies and lifetimes. It is reasonable to assume that our barriers contain some distribution of impurity levels. Combescot[15] shows that the most drastic influence on the tunnel conductance is obtained when one considers a distribution of resonant levels close to the Fermi level with impurities clustered within a few atomic planes.

If oscillations shown in the previous figures are due to above mechanism then the resonant levels we observe must be nearly equally spaced in energy. In the vicinity (and above) the longitudinal phonon emission threshold of[16] Mg the regularity of the structure decreases, this may be due to interference effects between the competing resonant and inelastic tunneling channels.

The lifetime broadening of atomic levels (of the order of 1 meV) gives an estimate of the localization time of an electron inside the potential well ($\sim 6 \times 10^{-13}$ sec). This time is comparable to the magnitude of barrier transmission times.[17]

On this basis the observed annealing effects are due to migration of impurities within the barrier. Insofar as the oscillations change in character with annealing they represent migrations which remain near the interface. Junctions in which annealing destroys the oscillations would indicate migration away from the barrier interface. Such migratory behaviour could be induced either thermally or by the application of the electric field.

In Fig. 8 typical results of the effect of a magnetic field (parallel to the tunneling current) on a junction shown in Fig. 6 are shown. The second set of data were obtained using a sensitivity 10 times greater than that used to obtain data in Fig. 6. The smaller amplitude of the oscillations in Fig. 8 is due to annealing effect. Figure 8 also shows the spin splitting of a level in the vicinity of 5 meV. This splitting yields a g factor of

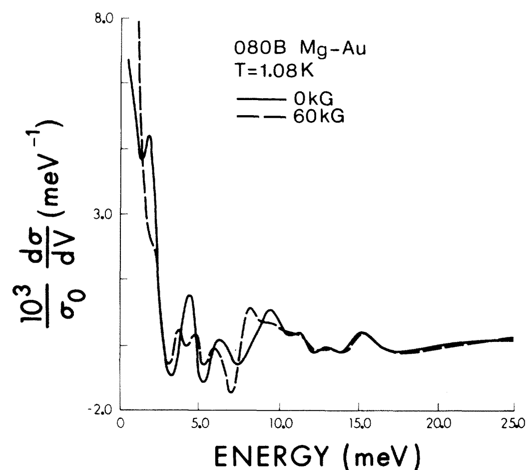

FIG. 8. Solid curve shows the junction shown in Fig. 6 after annealing and in the absence of a magnetic field (see text). The dashed line shows the effect of a 60-kG field parallel to the tunnel current: note that the inelastic peak due to longitudinal phonons in Mg at 16 meV is unchanged.

2.75. Furthermore Fig. 8 shows the field shifting and broadening of the oscillatory peaks, while the inelastic peak (due to Mg phonon near 16 meV) remains unaltered. Esaki *et al.*[18] reported similar observation of localized energy levels in the forbidden gap of PbTe.

Oscillations in tunnel characteristics of uracil-doped Pb-Pb junctions[19] were reported as well. Those were correlated with the uracil in the barrier assuming that the tunneling occurred through localized energy levels.

It should be noted that these observations appear in junctions regardless of choice of top electrode (Mg, Au, Pb, Bi). One can suggest two possibilities for the occurrence of required barrier impurities. These may have been introduced during the glow discharge process.[20] Alternatively our barriers may contain trapping centers due to nonstoichiometric oxide growth.[21] It is known that MgO can form a n-type semiconductor[22] where the donors occur due to the nonstoichiometry.

CONCLUSION

In this paper we have presented some observations of tunnel junctions in which we have seen a new oscillatory structure. The existence of the structure has been found to be independent of the top electrode (Mg, Au, Bi, Pb). The occurrence of the oscillations and their periodicity is independent of the thickness of electrodes. The variation of junction characteristics for samples prepared under identical conditions and their change with annealing led to a conclusion that metal-barrier interface is responsible for the appearance of the structure.

Arguments were presented which could account for the observed structure in terms of a resonant transmission of electrons through allowed energy levels existing in the barrier. Experiments in the presence of a magnetic field showed a splitting of some of the peaks, thus further indicating the atomic character of the levels. Unfortunately, it is impossible to determine the exact nature of the metal-barrier interface. We feel that defects and nonstoichiometry of the insulating barrier and possibly impurities within it cause the observed effects. In this connection we include the possibility of establishing a semiconducting transition region at the metal-insulator interface with band bending to screen out external charges at the metal-insulator interface. In such an interface Tsui[23] has shown that two-dimensional bands can be seen in tunneling experiments.

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