ULTRASONIC MAGNETIC RESONANCE OF ENHANCED NUCLEI USING THIN FILM TECHNOLOGY

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The Clarendon Laboratory, University of Oxford OX1 3PU, G.B.

Abstract. – We describe the fabrication of high efficiency thin film ultrasonic transducers for operation in the GHz frequency range and their subsequent application to the investigation of spin-phonon couplings and non-resonant dissipative processes in magnetic materials with enhanced nuclear moments.

The use of ultrasonic waves is well established as a tool for the investigation of the solid state and embraces such techniques as acoustic nuclear magnetic resonance and ultrasonic interferometry [1]. For the most part these studies employ discrete ultrasonic transducers of materials such as quartz which are bonded to the sample under study and operate at frequencies of order tens of MHz.

The experiments on enhanced nuclear magnetism described below represent the first application of these techniques at GHz frequencies and their success is due in no small measure to the fact that the acoustic transducers used were grown directly on the samples studied. This circumvents bonding and acoustic mismatch losses thereby allowing the use of much larger acoustic path lengths than are possible with bonded discrete transducers.

Among the many materials suitable for use as ultrasonic transducers in the low GHz frequency region, zinc oxide is an obvious choice on account of its high electro-mechanical coupling. Of the various deposition techniques available, sputtering of a zinc oxide target has yielded the most consistent and reliable results. The quality and efficiency of ZnO films decreases with longer sputtering times, apprently due to progressive misorientation of the piezo-electric axis during the sputtering process, and this limits the minimum practical operating frequency. This misorientation is also the major contributory factor to inefficiency in higher frequency transducers. Although transducer quality is highly sensitive to sputtering conditions these are not the only determining factors. It has been reported [2] that the character of the metallic films which precede the zinc oxide in order of deposition is of paramount importance and there is evidence to suggest that the overall transducer performance is controlled primarily by the character of the first film laid down. The experiments by Wagers *et al.* [2] revealed that flash evaporation yielded the best results in terms of the properties of the subsequent gold and zinc oxide films. Our experience suggests that the key to preventing this progressive degradation of the zinc oxide lies not only in flash metallisation but also in the establishment of a well-defined growth pattern at the start of the deposition by placing the substrate on the target in the region of large horizontal magnetic field and ion-scrubbing it vigorously prior to metallisation. Deposition of the films is started only when the partial pressures of water and organic contaminant have fallen below 10^{-7} torr. The substrate is covered with a flash of chrome followed immediately by a fast-evaporated 200 nm film of gold. The deposition surface is positioned over the target with the normal to the surface oriented at an angle of about 20° to the direction of incidence of sputtered material. The chamber is backfilled with a 50/50 Argon/Oxygen mixture to a pressure of 10 millitorr and the discharge is struck. After four minutes sputtering to clean the target, the substrate is uncovered and exposed to sputtered material for 20 minutes. The target substrate distance is 3 cm and the rf power is 200 W into a 10 cm diameter magnetron with a 5 cm diameter active ring. After the ZnO deposition, the rf is turned off and the substrate left to cool for 1 hour in 10 millitorr of Argon/Oxygen. Vacuum is broken to position the topdot mask which consists of a copper foil with an array of photoetched 0.3 mm diameter holes. The chamber is again pumped to base pressure and the Meissner trap refilled before evaporating the gold topdots onto the transducers. Connection is made to these topdots by ballbonded 30 micron diameter gold wires. The efficiency of the resultant transducers probably approaches 100 % at liquid helium temperatures since the bandgap impurity states are frozen out: however this is concealed by impedance mismatch between transducer and cryogenic downlead which introduces two-way insertion losses of 20-30 db depending on operating frequency. The transducers have roughly equal amounts of transverse and longitudinal piezo-electric activity (Fig. 1). Unlike some previous workers, we have not found it necessary to introduce organic contaminant into the chamber in order to promote transverse transducer activity and we rely totally on varying the deposition angle to control the amount of transverse action. This may not be in conflict with previous literature if the residual organic impurity in the chamber (which is of order

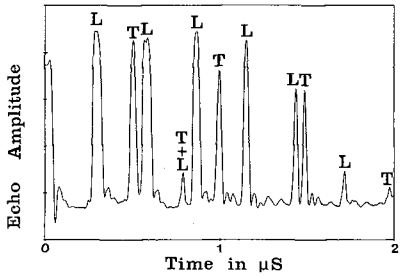

Fig. 1. – Ultrasonic echo train produced by a thin film transducer deposited with its piezoelectric axis at 20° to the normal. Note the echo "L + T" which results from mode conversion at the transducer.

10^{-8} torr) is sufficient to perform this function. Figure 1 illustrates the activity of a typical transducer. Note the echo labelled L + T which results from partial mode-conversion of the first longitudinal and the first transverse echoes into pulses of the other polarisation which arrive together at the transducer after the second round trip.

Acoustic resonance in enhanced nuclear paramagnets like Holmium Vanadate ($HoVO_4$) proceeds by a novel mechanism [3, 4] involving the magnetic hyperfine operator with the consequence that the signals observed are about eight orders of magnitude stronger than those obtained by conventional nuclear acoustic resonance. Acoustic attenuation is caused by the absorption of phonons at the nuclear resonant frequency by an "intrinsic direct process" similar to those by which thermal phonons induce spin-lattice relaxation and the attenuation coefficients at GHz frequencies and liquid helium temperatures can be as high as 10^2 m^{-1}. The value of the spin-lattice relaxation rate for the "intrinsic direct process" may thus be deduced in a temperature region where the relaxation is dominated by faster processes such as Orbach relaxation or relaxation by paramagnetic impurities.

The sample onto which the zinc oxide transducer is grown is polished to form an acoustic resonator. Measurements are made by observing the decay of the echo train resulting from excitation by a single ultrasonic pulse. The system operates over the bandwidth of the transducer (typically an octave) thus avoiding the problem of making a tunable low temperature instrument. Moreover, the frequency range of operation (0.5-6 GHz) fills in a traditionally awkward gap in the frequency spectrum which coincides with the majority of rare-earth hyperfine splittings. The amplitude of a particular ultrasonic echo as a function of applied magnetic field decreases on nuclear resonance owing to increased ultrasonic attenuation. This attenuation varies as the fourth power of the operating frequency and reciprocally with temperature. Cross-terms in the hyperfine interaction permit $\Delta M = 2$ resonances which are substantially weaker than the $\Delta M = 1$ type and vary in strength as (frequency) [2].

Besides the resonant nuclear ultrasonic absorption, there is a Debye style absorption mechanism associated with the doublet first excited state in $HoVO_4$ which couples to [100] longitudinal waves. The acoustic strain splits the doublet, thereby changing its effective temperature and the resulting relaxation between the two components gives rise to an acoustic loss mechanism which scales as $\omega^2\tau/\left(1+\omega^2\tau^2\right)$ where ω is the ultrasonic frequency and τ is the relaxation time. The value of the Orbach relaxation rate is deduced from this data to be 8 ∓ 1 GHz at 4.2 Kelvin. This non-resonant attenuation reflects the population of the excited doublet and hence it increases exponentially with rise in temperature. The attenuation decreases on application of a magnetic field at constant temperature which may be modelled to high accuracy by taking into account the convolution of several effects: a) the composition of the doublet changes with field and hence so do the ultrasonic matrix elements; b) the doublet population decreases with field because the singlet ground state energy is lowered quadratically; c) the relaxation rate is closely related to the Orbach rate between ground singlet and excited doublet which depends on the composition of the states concerned and therefore is a function of field.

[1] See for example Luthi, Moran, T. J. and Pollina, R. J., *J. Chem. Phys. Sol.* **31** (1970) 1741 and Ref. contained therein.

[2] Wagers, R., Kino, G., Galle, P. and Winslow, D., *Proc. IEEE Ultrasonics Symp.* (1972) 194.

[3] Bleaney, B., *et al.*, *Proc. R. Soc.* **A388** (1983) 479.

[4] Bleaney, B., *et al.*, *Proc. R. Soc.* **A416** (1988) 63.