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Acoustic Anomalies in Amorphous Thin Films of Si and SiO_2

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The ultrasonic absorption and variation of the sound velocity have been measured in sputtered films of amorphous silicon and amorphous silicon oxide from 0.5 to 300 K at a frequency of 300 MHz. A Rayleigh surface wave propagating along the surface of a piezoelectric crystal, which is covered by a thin film of amorphous SiO_2, allows a measurement of the well-known acoustic anomalies originating from two-level tunneling systems. In clear contrast, films of *a*-Si do not exhibit these typical anomalies.

The well-known anomalies[1,2] of the acoustic properties of amorphous materials at very low temperatures have been attributed to the scattering of sound waves by certain low-energy excitations in the disordered solid. A very successful phenomenological description[3,4] has been given in terms of two-level tunneling systems (TLS) which have a broad distribution of energy splittings. It is of particular interest to know whether these TLS are also present in amorphous solids which can only be prepared in film form. Notable among these are amorphous Si and Ge, as well as many of the metallic glasses.

Acoustic measurements require in general sizable sample dimensions, which excludes the study of thin amorphous films by conventional ultrasonic techniques. The acoustic properties of a film deposited on a suitable substrate can, however, be studied by means of surface acoustic waves (SAW). The effects of such films on surface-wave propagation have been studied extensively, primarily at ambient temperature.[5] Recent studies by Hartemann, Doussineau, and Levelut[6] and Haumeder, Strom, and Hunklinger[7] demonstrated that the surface-wave technique is useful even below 4.2 K. Furthermore, low-temperature dielectric measurements have been performed by Golding, Graebner, and Haemmerle[8] on *a*-Si films at frequencies $\sim 10^3$ Hz. However, no low-temperature acoustic properties have been previously reported for amorphous silicon films which were deposited onto surface-wave devices.

We present here the first measurement of the low-temperature acoustic properties of sputtered amorphous films of Si, $SiO_{0.7}$, and SiO_2. Our results provide evidence for the lack of TLS in sputtered amorphous Si films. The results further demonstrate that the acoustic properties of thin sputtered films of SiO_2 are similar (but not identical) to those of bulk glassy SiO_2.

The experiments were carried out on polished *YZ*-cut $LiNbO_3$ surface-wave devices with interdigital transmitting and receiving transducers spaced 10 mm apart.[9] Using water-cooled substrates, thin films of Si, $SiO_{0.7}$, and SiO_2 were sputtered from a Si target in a hydrogen-free argon atmosphere of 1×10^{-2} Torr (with oxygen partial pressures of 1×10^{-4} Torr for $SiO_{0.7}$ and 2×10^{-3} for SiO_2; background pressure 1×10^{-6} Torr) onto the entire space between the transducers. The films have been checked by x-ray diffraction to be fully amorphous. An identical surface-wave path on the same substrate was left without a film in order to eliminate the contribution of the crystal differentially. The variation of the attenuation and sound velocity in the deposited films were measured at temperatures between 0.4 and 300 K at a frequency of 300 MHz employing standard ultrasonic techniques.

In Fig. 1 the temperature-dependent absorption (after subtraction of the residual absorption at 0.4 K) is shown for three representative amorphous films of approximately 1-μm thickness. We discuss first the curve obtained for *a*-SiO_2

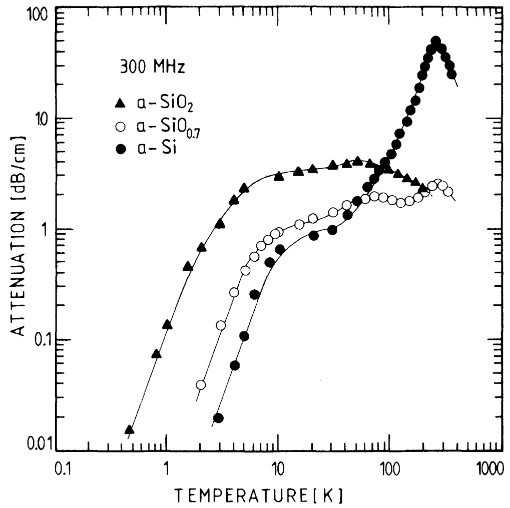

FIG. 1. Variation of the ultrasonic absorption vs temperature for three SiO$_x$ ($0 \leqslant x \leqslant 2$) films. The residual absorption has been subtracted.

since it can be compared with bulk values. The double-peak structure is characteristic of glassy SiO$_2$ and exhibits a large maximum at around 50 K.[10] In the bulk material this peak—though much more pronounced—is observed at about 60 K and has been previously interpreted by Anderson and Bömmel[11] as due to the thermally activated relaxation of structural defects. One possible defect that has been proposed in an oxygen atom which has two possible equilibrium positions either transverse[11] or parallel[12] to the Si-O bond direction. In addition, more complex structural units like SiO$_4$ tetrahedra[13] have been discussed. The large width of this peak can be explained in terms of a Gaussian distribution $P(V)$ of activation energies V caused by the randomness of the amorphous network. In the thin-film regime ($kh \ll 1$, where k is the Rayleigh wave vector and h the film thickness), the ultrasonic absorption due to thermally activated relaxation of defects can be evaluated as

$$\alpha(T) = \frac{\bar{K}_{\mathrm{SAW}}^2 Ikh}{4\rho v^3 k_{\mathrm{B}} T} \int_{V=0}^{\infty} dV\, P(V) \frac{\omega^2 \tau}{1+\omega^2\tau^2}$$

$$= \alpha_{\mathrm{bulk}} Ikh, \tag{1}$$

where $\tau = \tau_0 \exp(V/kT)$; ρ is the mass density of the film, and $\omega/2\pi$ is the frequency of the sound wave with velocity v. The deformation potential $\bar{K}_{\mathrm{SAW}}$ describes the coupling of defects responsible for the 60-K peak to the surface wave and is estimated to be of the order of 1 eV. The factor Ikh relates the absorption in the bulk to that in the film. It takes into account the fact that only a fraction of the energy is propagating in the film. The frequency dependence of Ikh is due to the wave vector $k = \omega/v$; the factor $I < 1$ is frequency independent and is only a function of the elastic constants of the film material. A fit of Eq. (1) to the surface-acoustic-absorption spectrum of a sputtered glassy SiO$_2$ film leads to an activation energy V of about 40 meV with a considerably (~ four times) broader distribution $P(V)$ than the bulk.

On cooling, a shoulder has been observed in bulk a-SiO$_2$ at a temperature of ~ 10 K for which another relaxation process is responsible involving only TLS. Figure 1 shows a corresponding shoulder for the three films we investigated. An incident surface acoustic wave with angular frequency ω alters the level splitting of the TLS and thus disturbs the thermal equilibrium population. The TLS relax to thermal equilibrium via phonon-assisted tunneling.[4] The absorption resulting from this relaxation process is given by

$$\alpha(T) = \frac{\bar{D}_{\mathrm{SAW}}^2 Ikh}{\rho v^3} \int_0^{\infty} dE\, n(E) \frac{df(E)}{dE} \frac{\omega^2\tau}{1+\omega^2\tau^2}, \tag{2}$$

where $f = [1 + \exp(E/k_{\mathrm{B}}T)^{-1}$; $\bar{D}_{\mathrm{SAW}}$ is the averaged deformation potential of the TLS and $n(E)$ their density of states. The corresponding relaxation time is found to be[4]

$$\tau^{-1} = \frac{\bar{M}_{\mathrm{SAW}}^2}{\rho v^5} \frac{E^3}{2\pi\rho h^4} \coth(E/2k_{\mathrm{B}}T). \tag{3}$$

Here $\bar{M}_{\mathrm{SAW}}$ is the elastic coupling constant describing the induced transitions between the two states. The bar expresses the average over the longitudinal and transverse polarization. The above equation is essentially identical to the case of bulk phonons interacting with the TLS, since the wavelength of the phonons (~ 1000 Å for $T = 1$ K), which dominate the TLS lifetime, is much less than the film thickness. At the lowest temperatures of our experiment the absorption strongly increases with temperature as predicted by Eqs. (2) and (3) for the case of $\omega\tau \gg 1$. In this limit the magnitude of the absorption at a fixed temperature is only determined by the density of states n and the elastic coupling parameters $\bar{D}_{\mathrm{SAW}}$ and $\bar{M}_{\mathrm{SAW}}$:

$$\alpha \propto n \bar{D}_{\mathrm{SAW}}^2 \bar{M}_{\mathrm{SAW}}^2. \tag{4}$$

If we compare the low-temperature absorption of our three films a strong decrease of the magnitude of α with decreasing oxygen content is observed. Thus, either the density of states of TLS or their coupling to surface acoustic modes scales with the oxygen content, neglecting possible differences in the distribution of the tunneling parameters.

Simultaneously with decreasing oxygen content the high-temperature peak at 50 K diminishes and instead a new and even stronger peak appears at about 270 K. This peak is the dominant feature in the a-Si film. Fitting the data with a Gaussian distribution of activation energies and with the assumption that $\tau_0 = 10^{-13}$ sec as in bulk a-SiO$_2$, leads to a distribution of activation energies in a-Si which is centered at 0.176 eV (40 meV for a-SiO$_2$), i.e., the activation energy is roughly four times larger than in a-SiO$_2$. The spread in the activation energy is of the order of 32 meV for a-SiO$_2$, as well as a-Si. The occurrence of this relaxation peak in a-Si is extremely surprising. A fourfold-coordinated network such as that of a-Si should not allow motions similar to that of the twofold-coordinated oxygen atom in a-SiO$_2$. The well-established existence of voids in sputtered or evaporated a-Si allows a possible explanation. Thermally activated structural relaxation of Si atoms on the reconstructed internal void surfaces[14] may be responsible for the 270-K peak in the surface acoustic absorption. As initial small amounts of oxygen (< 1 at. %) are added to a-Si they will most likely be incorporated in the void surfaces. This process leads to a strong reduction of the intrinsic Si acoustic-absorption peak, but does not lead to a corresponding increase of the absorption at ~ 50 K associated with SiO$_2$. At higher concentrations, SiO$_2$ bonding configurations develop in the bulk structure of the Si film leading to an increase of the ~ 50-K peak as well as the lower-temperature tunneling contribution. The present results support the previous assumption that the relaxing particle in a-SiO$_2$ is a single oxygen atom. If the relaxing particle were more complex, a gradual shift of the absorption peak from 50 K in a-SiO$_2$ to 270 K in a-Si would be expected, reflecting the gradual change in the composition of the moving unit. The existence of two distinct absorption maxima in a-SiO$_{0.7}$ supports this interpretation.

In Fig. 2 the temperature variation of the SAW velocity is plotted for a-SiO$_2$ and a-Si films. Whereas a relatively strong temperature dependence is observed in a-SiO$_2$ below 10 K, no variation is found in a-Si within the accuracy of our measurement. This logarithmic increase of the velocity is characteristic of glasses and is due to the *resonant* interaction between the TLS and the sound wave.[15,16] (There is also a contribution to the absorption due to this resonant interaction which is not observed in the SAW experiment due to power saturation effects.

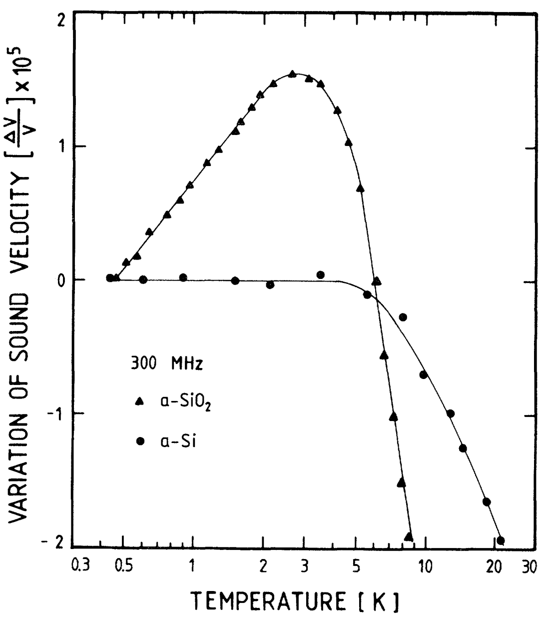

FIG. 2. Variation of the sound velocity for 1-μm-thick films of a-Si and a-SiO$_2$.

In a thin amorphous film of thickness h the logarithmic increase in the velocity of SAW of wave vector k can be evaluated to be[17]

$$\frac{\Delta v}{v} = \frac{n_0 \bar{M}_{\mathrm{SAW}}{}^2 I}{\rho v^2}\left(k_l h \ln\frac{T}{T_0}\right), \tag{5}$$

where $k_l = \omega/v_l$, v_l being the longitudinal velocity of sound of the film material. T_0 is the arbitrary reference temperature ($T_0 = 0.44$ K in our case) which defines the zero of $\Delta v/v$ and n_0 is the density of states which is assumed to be constant for small energy splittings. For a value of $Ikh = 0.036$ we deduce[18] $n_0 \bar{M}_{\mathrm{SAW}} = 1.8 \times 10^7$ J/m^3 in the a-SiO$_2$ film which is comparable to $n_0 M_l{}^2 = 2.3 \times 10^7$ J/m^3 obtained for longitudinal waves in bulk a-SiO$_2$.[2] For the a-Si film we can give an upper limit: $n_0 \bar{M}_{\mathrm{SAW}}{}^2 < 1.5 \times 10^6$ J/m^3, i.e., 12 times *smaller* than for the a-SiO$_2$ film. This small value is in agreement with the absorption data obtained at low temperatures, where the absorption due to the the relaxation of TLS was found to be considerably smaller than in the a-SiO$_2$ film. Two explanations seem to be possible. Firstly, the coupling $\bar{M}$ of the TLS to the network and consequently $n_0 \bar{M}^2$ could be extremely small. Secondly—and in our view more likely—there are no TLS at all in an "ideal" (void- and oxygen-free) a-Si film.

This is consistent with a random-network calculation by Smith[19] which demonstrates the difficulty of achieving double-well potentials of low asymmetry in a fully fourfold-coordinated network. In this case the small relaxation absorption observed in a-Si (see Fig. 1) at low temperatures would probably be caused by residual oxygen impurities incorporated in the a-Si film during the sputtering process or by a small subset of defect states on interior void surfaces.[20] The lack of TLS in the fourfold-coordinated network of a-Si supports the suggestion: The higher the coordination number of a material, the lower the number of low-energy excitations present in covalently bonded amorphous materials.

In summary, we have demonstrated the first successful application of high-frequency surface-wave techniques to the study of low-temperature properties of thin amorphous films. The acoustic absorption of sputtered SiO_2 was measured, and was found to be similar to that of bulk a-SiO_2. With decreasing oxygen content of the film the high-temperature absorption peak of a-SiO_2 disappears and a new peak at much higher temperatures arises. Most important is the observation that the magnitudes of the acoustic anomalies observed in SiO_x glasses at low temperatures are strongly reduced with decreasing oxygen content.

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