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INTERACTION OF ULTRASONIC PHONONS WITH DONOR IMPURITIES IN HYDROGENATED AMORPHOUS GERMANIUM

K.L. Bhatia* and S. Hunklinger

Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, D-7000 Stuttgart 80, F.R.G.

* On leave from: Department of Physics, Maharshi Dayanand University, Rohtak-124001, India

Abstract.- We have studied the propagation of acoustic surface waves at temperatures between 0.45 K and 475 K in hydrogenated amorphous germanium doped with phosphorus. At low concentrations a strong absorption maximum at 18 K is observed, whereas at high doping rates this absorption is suppressed. In similarity to crystals our results can be explained by the interaction between the sound wave and the degenerate donor ground state.

Introduction.- A current focus of interest in the field of amorphous semiconductors is the question of substitutional doping. The demonstration /1,2/ that amorphous silicon and germanium can be doped to exhibit n-type or p-type behaviour, has stimulated a variety of experimental and theoretical investigations /3/. Inspite of extensive experimental studies, the nature of donor or acceptor impurity states in doped a-Si:H and a-Ge:H remains far from being understood /3/. Study of these impurity states by ultrasonic methods can provide information about their dynamical properties. In this communication we report on experiments in phosphorous doped a-Ge:H by acoustic surface wave technique.

Experimental.- As substrates, we used standard yz-cut LiNbO₃ surface wave devices with interdigital transmitting and receiving transducers 10 mm apart. Thin films (thickness about 0.3 μm) of doped hydrogenated a-Ge were reactively sputtered onto heated substrates (substrate temperature was about 90 °C) in a mixture of Ar + PH₃. Whereas the pressure of hydrogen and total pressure of argon was kept constant at 1x10⁻³ and 5x10⁻³ Torr, respectively, the partial pressure of the mixture Ar + PH₃ (1.12% volume PH₃ in Ar) was varied to prepare films of different phosphorous concentration. No crystalline region in the film could be detected by X-ray diffraction. We estimate 3000, 20 and 10 ppm PH₃ in Ar in the sputtering plasma. It is known that in the doping regime approximately 20% of the impurity atoms enter /11/ substitutionally in the amorphous silicon network and rest as self-compensated sites. A reference surface wave path on the same substrate was left without a film in order to determine and to subtract the contribution of the LiNbO₃-substrate. Measurements of the attenuation with temperature were carried out between 0.45 K and 475 K at a frequency of 300 MHz.

The attenuation q_p of an acoustic surface wave propagating on a substrate which is covered by a thin film, is related to the attenuation q_f of a surface wave on a bulk sample of the film material by q_p = q_f + q_hk. I is a constant and depends only on the elastic properties of the substrate and the film, k is the wave vector and h the film thickness. This relation is valid if the penetration depth of the surface wave is much larger than the film thickness, i.e. if kh << 1/4. From our measured absorption we subtract the "residual" attenuation estimated from the leveling off of the absorption at the lowest temperatures. In all our plots we show the value q_p/4kh, i.e. the attenuation estimated for a surface wave on the bulk material.

Results and Discussion.- In Figure (1), the normalized ultrasonic absorption of a-Ge(H,P) films of different P concentrations is shown as a function of temperature. Attenuation of 9 GHz ultrasonic waves in crystalline Ge(P) taken from reference /6/

* On leave from: Department of Physics, Maharshi Dayanand University, Rohtak-124001, India.
is also shown in Figure (1) (curve A). For comparison the attenuation in a-Ge(H) film, containing approximately the same amount of hydrogen as in the doped film 5/5, is plotted. The acoustic absorption in a-Ge(H,P) shows significant differences from that in a-Ge(H). For the sample E having the lowest phosphorus concentration (10 ppm) a strong and broad absorption peak is detected at 18 K which decreases only slightly with temperature above 20 K. The magnitude of the absorption is considerably enhanced if the concentration of phosphorus is increased to 20 ppm (sample D). A further increase to 3000 ppm (sample C), however, suppresses this strong absorption. Instead, the absorption rises linearly with temperature up to 30 K as in a-Ge(H) /5/. Above 30 K a steep rise of the absorption similar to that in a-Ge(H) is observed, but its onset is at a much lower temperature.

In seeking an interpretation it is worthwhile to discuss first the attenuation in crystalline germanium doped with phosphorous. In c-Ge(P) also a maximum in the ultrasonic absorption is observed around 20 K. It has been explained by the strong scattering of ultrasonic phonon by electrons bound to the donor impurities /6/. In crystalline germanium the donor ground state is four-fold degenerate due to the multi-valley nature of its conduction band. Because of the local field this degeneracy is lifted and the ground state splits into a singlet and a triplet state separated by 2.8 meV. An ultrasonic wave modulates the energy separation between the singlet and triplet ground states and thus disturbs thermal equilibrium. The impurity electrons try to reestablish equilibrium via transition between these states by emission or absorption of a thermal phonon. As usual, such a process leads to absorption of ultrasonic wave. In amorphous semiconductors the wave vector $k_e$ of the electrons does not remain a good quantum number because of the absence of long range order. The wave vector may become uncertain within a certain spread $\Delta k_e$. There is close similarity of the radial distribution function (RDF) in the amorphous and in the crystalline phases up to the second nearest neighbours /7/. Therefore spread $\Delta k_e$ in the wave vector is probably much less than the separation between the degenerate minima of the conduction band. In the theoretical considerations /8/ it has been argued that impurity states in amorphous semiconductors resemble in many ways the corresponding impurity states of crystalline semiconductors. There is, however, also an important difference: in amorphous materials impurity states and the localized tailing band states can be degenerate energetically. Therefore, an
electron can escape from the impurity by hopping to neighbouring localized states, leading to an intrinsic width of the impurity state due to its finite life time /9/. Furthermore, the band extrema might have undergone a change in the amorphous phase.

With these arguments in mind we believe that the donor states in amorphous germanium behave elastically similar to those in crystals. Probably the picture of four-fold degenerate donor states in 'a-Ge(H,P) may be visualized and a process like valley orbit interaction and the strain fields due to disorder of amorphous network may split the impurity ground states. In the absence of information about the symmetry of the band extreme, it may not be possible to fix the degeneracy and symmetry of the individual levels in the amorphous case. Ultrasonic wave modulates the energy separation between the split off levels and relaxation of impurity electrons between these states attenuates the wave.

In principle the ultrasonic attenuation due to a relaxation process is given by /10/:

$$\alpha = N D^2 \frac{3f}{\rho v^3} \frac{2\pi}{\omega I} \frac{\omega^2 T}{1 + \omega^2 \tau^2}$$ (1)

where $\rho$ is the mass density and $v_0$ the velocity of longitudinal sound waves of frequency $\omega/2\pi$. $N$ represents the number of relaxing centers, in our case the number of donors. $D$ is the deformation potential, reflecting the variation of the energy splitting between the relaxing states, due to the strain of the sound wave. The factor $3f/3E$ describes the variation of the population of the upper relaxing level with energy. Depending on the degeneracy $f$ is given by $f = n[n + \exp(E/k_BT)]^{-1}$, where $n = 1, 2$ or 3 and $E$ is the energy splitting between the relaxing centers (in the crystal $E = 2.8$ meV). The relaxation time $T$ reflecting the transition probability of the electron can in principle also be written down, but the deformation potential for this process is not known. Furthermore the randomness of the amorphous structure leads to a distribution of not only the level splitting $E$ but also of the coupling parameters. Therefore no quantitative fit of the experimental data can be carried out so far.

It is surprising that at high phosphorous concentration (sample C) the strong absorption due to the relaxation effect is suppressed. The reason lies probably in the fact that with increasing impurity concentration the wave functions of neighbouring impurities overlap more and more until finally an impurity band is formed. In the latter case we cannot speak of separate states and a relaxation process in the original sense is not possible anymore. At higher temperatures ($T \geq 30$ K), the structural relaxation of hydrogen atoms attached to the phosphorous impurities may contribute to ultrasonic absorption like in a-Ge(H), but no direct evidence for such a process is known so far /5/.

In summary, we have studied the interaction of ultrasonic surface phonons with the donor impurities in a-Ge(H,P) down to 0.45 K. Strong influence of the impurity concentration on the ultrasonic attenuation has been observed. Presence of a broad absorption peak at about 10 K followed by a strong absorption continuing to higher temperatures is revealed in films of lower donor concentrations. At higher donor concentrations this attenuation peak is suppressed. Instead, a steeply rising attenuation at higher temperatures appears. We propose that the donor ground state in a-Ge(H,P) may be thought to have a degeneracy like in c-Ge(H,P) due to the multi-valley nature of the conduction band. A process like valley orbit interaction and disorder induced internal strain fields may lift the degeneracy of the donor ground state. This process becomes inactive as soon as an impurity band is formed.

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References