NARROW BAND GAP SEMICONDUCTORS AS
ACOUSTIC PHONON TRANSUDERS

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It's actually with some considerable apprehension that I address this audience. I will try to alleviate my apprehension somewhat by telling you right at the outset that I do not have a single data slide showing a detected flaw. What's more I have to confess, I have never detected a flaw. I sincerely hope you'll forgive me for this. My apprehension is heightened by my observation over the last several days that there is very little interest in ultrasonic work at the frequencies that are of interest to me, the range of about 1 to 10 GHz. I don't think I've heard anything over 1 GHz mentioned. Perhaps it's becoming apparent to most of you that I am not principally in nondestructive evaluation. What I am interested in is lattice dynamics; more specifically relaxation effects in dielectric solids.

Now, where I hope there is some convergence of our interests is in the area of transducers. Let me describe to you typically the sort of sample that I would be concerned with. It would consist of a piece of plastic dielectric. The source of the ultrasonics is within the sample and consists of dispersed phonon radiators which, depending upon the experiment we are doing, are radiating ultrasonics within a very narrow band width of only a megahertz anywhere from as low as 25 MHz to 10 GHz.

Now, what is clear is we cannot use a piezoelectric detector bonded to the surface of this material. The radiating sources, acoustic radiators, I'll call them, have no phase relationship between them. They're each radiating independently and consequently, there's no coherent wave front at the surface to produce an output signal from a piezoelectric device.

What I've been concerned with for a short period of time now, is developing a sensitive, low noise transducer, which is an incoherent quantum detector for acoustic phonons in the 25 MHz to 10 GHz range.

If you go to the solid state physics literature, you will find that there are quite a variety of schemes for quantum counting acoustic waves. Largely, these are very complicated schemes that require coupling of an acoustic phonon to an electromagnetic wave and monitoring the absorbed electromagnetic power at radio, microwave or optical frequencies.

If your application is compatible with any of these methods, you can achieve quite good signal-to-noise by quantum counting. Because of our particular application we needed a fairly simple detection scheme, so we started looking at the possibilities of using narrow band gap semiconductors as quantum detectors for elastic waves in dielectric lattices.
I have illustrated in Fig. 1 the conventional Brillouin zone picture for a semiconductor, in the reduced Brillouin zone scheme. We have filled valence band and a fast conduction band which, for an intrinsic semiconductor, is unpopulated at sufficiently low temperatures. Such a semiconductor would be characterized by the direct band gap $\varepsilon$. In Fig. 1, I have also drawn an acoustic absorption spectrum for the semiconductor, which would be similar in appearance to the electromagnetic absorption spectrum. The absorption spectrum obviously would have a cutoff at the frequency corresponding to the direct band gap. This would be true for either electromagnetic absorption or for acoustic phonon absorption. The band gap then defines the useful cutoff frequency for detection, in single quanta, of elastic waves.

There is a slight difference between absorption of an elastic wave and absorption of an electromagnetic wave, which is worth mentioning. A phonon of the same frequency as a photon has considerably more momentum. Consequently, while only vertical transitions in this scheme are permitted for photons, we must consider non-vertical transitions involving transfer of wave vector concomitant with the absorption of phonons. What this means, practically, is that since the tabulated values of semiconductor band gaps are determined by electromagnetic absorption, the appropriate value for elastic wave single quantum absorption may be, in fact, considerably lower as I've indicated in Fig. 2.

The first thing that one discovers upon looking into this further is that the very narrowest band gap detectors available operate far above ultrasonic frequencies. One must look for some way of effectively narrowing the band gap in order to develop an acoustic phonon quantum counter. One way to achieve this goal, of course, is to try and dope the semiconductor lattice in some fashion to create localized states between the conduction band and the valence band as illustrated in Fig. 3. It is possible to introduce donor states which will lie below the conduction band and acceptor states, lying a little above the valence band.

In principle, an elastic wave would directly excite one of the acceptor states leaving behind a hole which would then be accelerated in the applied field. Ultimately that hole would be annihilated by combination of the thermally populated acceptor state, regenerating the acoustic wave. One would have detected the passage of the acoustic wave by a momentary change in the conductivity of the detector. However, examination of acceptor and donor localized energy levels of common impurities indicates that these levels are not accessible energetically to direct excitation by ultrasonic waves.

Practically speaking, you cannot find a suitable donor that will introduce localized levels energetically accessible at ultrasonic frequencies. We turned next to the idea of creating semiconductor alloys. Some of you may be familiar with this. If you take two semiconductors characterized by two different direct band gap and form binary alloys, the discrete band structure doesn't disappear, but varies linearly as a function of composition. The best known of these alloys is mercury cadmium telluride, the composition of which may be written as $\text{Hg}_x\text{Cd}_{1-x}\text{Te}$. Mercury telluride accurately is not a semi-
Fig. 1. Energy band diagram for a direct band gap semiconductor with corresponding absorption spectrum.
Fig. 2. Energy band diagram for an indirect band gap semiconductor with corresponding absorption spectrum.
Fig. 3. Energy band diagram for semiconductor with localized states between the valence and conduction bands.
conductor by itself but rather a semimetal. It may be thought of as a semi-conductor with a negative band gap. It has been established that both density and lattice constant are nearly linear functions of the variable $x$ for this alloy. In fact, when you look at the direct band gap between the fast conduction bands and the localized valence bands you find that that's also a fairly linear function of composition between the two end point compounds. Since in this case one of those compounds is a semimetal, the band gap goes through 0 and our idea, very simply, was to obtain a phonon quantum counter in an alloy semiconductor in the region of zero-band-gap composition. The problem with this approach is that the compounds are absolutely miserable to work with; they are rather soft and the alloy is hard to polish; they have to be grown in ingots and then lapped very carefully.

We decided to try an alternative approach, and that is narrowing the band gap by altering the semiconductor structurally rather than chemically. One can introduce progressively greater amounts of disorder into an ordered pure semiconductor. Let me refer you to Fig. 4 in which I have illustrated, in a reduced Brillouin zone scheme, the energy of a free electron as a function of its wave vector. As one introduces periodicity into the lattice, you start to get standing wave contributions to the wave function solutions at the boundaries of the Brillouin zone with the result that band gaps appear in the region of the Brillouin zone boundary and $k = 0$ as illustrated for a perfectly ordered lattice, by the dashed lines.

In a very qualitative fashion then, if you started with a perfectly ordered lattice and introduced progressively more disorder, you would tend to narrow the forbidden band gaps. Aperiodicity can be introduced in two ways. It may be introduced by allowing the spacing to fluctuate. You can then solve the wave equation in a disordered coordinate. What you’ll get back is the original wave equation plus some perturbation terms. The end effect is that the gap between the valence band and the conduction band is narrowed. The other part of the disorder would come in fluctuations of the well depth shown and that would tend to introduce localized levels within the band gap, very much like the donor and acceptor states of an impurity semiconductor. Combining the two, then, we would have a narrowed band gap, which is what we want, with some localized states within the band gap.

Some theoretical calculations are available for the integrated density of states per unit chain length for various degrees of disorder in a semiconductor which indicate that, as progressively more and more disorder is introduced into the structure, the band edges first round off, and then more and more states start to appear within that band gap. We evaporated germanium film into a cold substrate to get the maximum amount of disorder in the initial amorphous structure. Then by progressive annealing cycles we reintroduced order until we obtained the response to ultrasonics that we wanted. So, we start with a completely disordered structure and we anneal in some order in an attempt to get the rather large intrinsic band gap of germanium down to a level where we can detect gigahertz ultrasonics.

We did test one of these thin film incoherent ultrasonic detectors. We bonded it using a silicon grease bond to an aluminum test block and then simply attempted to detect 1 GHz ultrasonics in the block generated by a thin film
Fig. 4. Energy band diagrams showing effects of lattice disorder.
zinc oxide piezoelectric transducer. The results are presented in Fig. 5 which shows the output of the detector versus the frequency of the ultrasonics which we swept over a small range. All of the structure that you see comes from standing ultrasonic waves within the sample and evidently, the detector substrate on which the germanium thin film incoherent detector was built.

Thank you very much.
Fig. 5. Response of germanium thin film incoherent ultrasonic transducer.
DISCUSSION

DR. BERTONI: Any questions?

DR. DON THOMPSON (Rockwell International Science Center): With respect to your three phase alloys, did you find them stable enough to lower the band gap towards zero and remain in that condition for sometime?

PROF. FRANCIS: No, I got instantly discouraged and went to trying disorder to narrow the band gaps. It's hard to get homogeneity in the band gap and it varies somewhat with temperature. They're stable enough so that you can make graded detectors. That is, you can change the composition as you go deeper into the detector, so that, looking into the detector, the band gap is narrowing or opening, but there's a lot of technology involved.

DR. BERTONI: Is there a question over here?

DR. LLOYD GRAHAM (Rockwell International Science Center): One immediate application for these is in detection of very low level acoustic emission signals which are generated during deformation and fracturing of solids. The question is, what is the acoustic power that you used in your work?

PROF. FRANCIS: About 1/10 of a microwatt. Ultimately, since the signal to noise is very good, you could anticipate very low detection limits.

DR. ROBERT THOMAS (Wayne State University): My recollection of the literature on amorphous germanium was that you have rather sharp band edges. Are you saying that the band gap actually goes to zero in amorphous germanium?

PROF. FRANCIS: Well, you recall the integrated density state curves I showed.

DR. THOMAS: Was that experimental or--

PROF. FRANCIS: It was calculated. My evaluation of them was that they were quite reasonable.

DR. THOMAS: There has been a lot of activity in the amorphous area in recent months.

PROF. FRANCIS: Probably a lot more theoretically.

DR. THOMAS: Experimentally as well. My understanding was that you still have the band gap, but maybe somebody else--

PROF. FRANCIS: If I draw your attention to this curve, within the limits of this theory...

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DR. THOMAS: Right. But the theory is not at all well understood, at the moment, on amorphous materials. It is a very open question.

PROF. FRANCIS: Right. So, we took very much an empirical approach. It looked like it might work, and we obtained sensitivity after annealing the films a bit that suggests to us that we had narrowed the band gap to the point where we were looking at acoustic quantum transitions...

DR. THOMAS: You saw signals, but are you sure that's coming from innerband transitions? I doubt it.

PROF. FRANCIS: Well, there might equally well be a percolation effect between localized states; a "hopping" model might be more appropriate...

DR. BERTONI: Another question back here?

PROF. Krumhansl (Cornell University): A simple experimental question. The curves you showed of the standing wave signal, there would seem to be a frequency range of about 2 percent. Yet over that frequency range there's about a 2 to 1 variation in the average amplitude. Was that strictly instrumental?

PROF. FRANCIS: It's due to the impedance matching of the zinc oxide transmitting transducer which varies with frequency.

PROF. Krumhansl: So, the effect should be very broad then.

PROF. FRANCIS: Oh, yes. We have gone down to 25 MHz. Any change we see is centered in the generating transducer.

DR. SY FRIEDMAN (NRSD, Annapolis): What does one detect when one detects?

PROF. FRANCIS: What was the signal?

DR. FRIEDMAN: Yes. Is it the variation in the conductivity of the germanium?

PROF. FRANCIS: Yes.

DR. ED KRAUT (Rockwell International Science Center): You mentioned at the beginning of your talk that you had these nice little radiators distributed all throughout the dielectric block. What are they?

PROF. FRANCIS: They're a variety of things depending on what sort of acoustic wave we want to produce; paramagnetic spins in very low concentration; chips of piezoelectric might be used; little flecks of zinc oxide for example.

DR. KRAUT: You have all of these or some of these?

PROF. FRANCIS: Those are some of the possibilities. In any given case we would have just one source.
DR. KRAUT: In any given case we would have just one source. Did you actually distribute these things?

PROF. FRANCIS: Yes, oh, surely. Those are typically the sort of problems we deal with, where the signal is distributed at a lot of point sources throughout the material. We're looking at relaxation phenomena like spin-lattice relaxation. Now, at low temperatures, the phonons that are generated by a relaxation process are bottlenecked very narrowly about the characteristic frequency associated with the relaxation event.

MR. JOHN BRINKMAN (U.S. Army Armament Command): Aren't you really talking about the kind of electron phonon interactions that people talk about in superconductors and also about the same kind of band gap?

PROF. FRANCIS: Yes. We examined detection schemes using superconducting bolometers. It's a question of time response.

MR. BRINKMAN: Wouldn't this be essentially the same thing if you were successful in it?

PROF. FRANCIS: Yes, but faster.

MR. BRINKMAN: This is faster, okay.

PROF. FRANCIS: Much faster.

DR. BERTONI: I have one question. Can you use this to acoustically control the optical reflectivity from the surface of this material? In other words, by acoustic energy, to put more electronic energy into the conduction band and increase the reflectivity. Is there a possibility in this?

PROF. FRANCIS: I don't think you're putting an awful lot of free charge carriers up into the conduction band, not in the way we conduct the experiment. Now, maybe with a great amount of power you might do this.

PROF. HARRY TIERSTEN (Rensselaer Polytechnical Institute): How do you excite these individual centers?

PROF. FRANCIS: One way would be just to apply an electromagnetic field which is resonant with paramagnetic spins.