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STRUCTURAL PROPERTIES OF AMORPHOUS
SEMICONDUCTORS BY MOSSBAUER SPECTROSCOPY

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A. SUMMARY

Comparison of the ^{125}Te Mössbauer spectra in amorphous and crystalline Te films indicates that in the amorphous phase the quadrupole splitting is about 20% greater and the recoil-free fraction about one-third as great as in the crystalline phase. The increase in quadrupole splitting is interpreted as indicating a decrease of about 3% in the length of the covalent bond between the nearest neighbor Te atoms in the amorphous state. The decrease in recoil-free fraction in the amorphous film is explained as due to dangling bonds at the ends of the Te chains which are responsible for a change in the density of phonon states in the system.

A short paper covering this work has been prepared for submission to Solid State Communications and is included as an Appendix to this report.

As mentioned in the last Semi-Annual Technical Report, a weak source of ^{125}Te in $\beta\text{-TeO}_3$ proved to be a considerable improvement over the ^{125}I in Cu source we have been using. It is important that we obtain a better resolved spectrum of the amorphous tellurium film. To this end we have been attempting to prepare thicker films and also to obtain a strong source of $\beta\text{-}^{125}\text{TeO}_3$. We have improved the quality of our films and can now form amorphous films about 2μ thick

with a fair degree of reliability. The β -TeO₃ source has still proved to be an obstacle. Our most recent attempt to make a strong source ended in failure due to a difficulty in the chemical preparation. A new batch of ¹²⁵Te is being prepared in the reactor (by our supplier, New England Nuclear Corporation) and we are still hopeful of eventual success.

B. BACKGROUND

The necessary background was reported earlier in Technical Reports No. 1 and No. 2.

C. TECHNICAL PROGRESS

The results of our work to date are given in the manuscript submitted for publication to Solid State Communications and included as an Appendix to this Report.

D. FUTURE PLANS

The vacuum deposition apparatus has been slightly altered in order to improve the cooling of the samples during deposition. The deposition of amorphous films of the requisite thickness (~ 4 microns) is a delicate procedure which requires considerable experience and patience. We have recently made several films ~ 2 microns thick. The dramatic difference between the amorphous and polycrystalline sample spectra shows that we have succeeded in carrying out the principal objective of this program,

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namely: to show that the Mössbauer technique is useful for studying order-disorder transformations in solids. In order to obtain consistent and better resolved spectra, we shall need thicker uniform films possibly enriched up to 95% in ^{125}Te .

A further improvement in spectral resolution may be expected to result from our efforts to obtain a better Mössbauer source. The line width in ^{125}Te Mössbauer spectroscopy would greatly benefit all workers in the field of tellurium Mössbauer spectroscopy. We are thus continuing to investigate improved Mössbauer sources for the tellurium-125 spectroscopy. In particular, in collaboration with the New England Nuclear Corporation, we are evaluating a new method of preparing $\beta\text{-TeO}_3$ sources and the feasibility of using sources incorporating 2.7 year ^{125}Sb .

APPENDIX

MÖSSBAUER STUDY OF AMORPHOUS AND CRYSTALLINE TELLURIUM *

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Comparison of the ^{125}Te Mössbauer spectra in amorphous and crystalline Te films indicates that in the amorphous phase the quadrupole splitting is about 20% greater and the recoil-free fraction about one-third as great as in the crystalline phase. These changes are interpreted as indicating a decrease of about 3% in the length of the covalent bond between the nearest neighbor Te atoms in the amorphous state, and furthermore that dangling bonds at the ends of the Te chains are responsible for a change in the density of phonon states in the system.

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Amorphous semiconductors have received considerable attention in recent years both because of their potential technological importance and because of the challenges posed to solid-state theorists by their lack of long range order. Of all the semiconducting elements which give rise to a readily observable Mössbauer hyperfine structure, only tellurium satisfies the requirement of being easily prepared in an elemental amorphous form (1). The Mössbauer effect in bulk crystalline tellurium has been extensively investigated (2,3), so that the structure of the crystalline phase has been well characterized in terms of the Mössbauer spectra hyperfine structure parameters. Mössbauer studies of the amorphous to crystalline phase transitions in tellurium based glasses (4) and in amorphous selenium doped with 2% tellurium (5) have been recently reported. Because pure tellurium is an elemental system, complications associated with possible compositional disorder and phase separation are eliminated and the Mössbauer results should be amenable to a relatively straightforward interpretation.

At ordinary pressures tellurium is a semiconductor which crystallizes with space group D_3^4 or D_3^6 having three atoms per unit cell in a structure consisting of long parallel helical chains with overall trigonal symmetry. The neighboring atoms within the same chain are covalently bonded, while between chains they are connected by a somewhat weaker combination of van der Waals and metallic bonding. The

amorphous form, which probably does not have a unique structure unless the method of preparation is specified, may be prepared by evaporation in a vacuum onto a cold substrate. It has been reported that such an amorphous film crystallizes with a sudden change in morphology when warmed above about 285 K ⁽¹⁾. We have confirmed that films deposited in our laboratory in a manner described below do, in fact, undergo a rapid transformation at this temperature. The conductivity of Te films deposited on low temperature fused silica substrates was observed to increase irreversibly by about four orders of magnitude during an increasing temperature interval of about 1 K at 285 K. We take this to be an indication of the amorphous to crystalline transition. It is the purpose of this note to report the changes in the Mössbauer parameters in going from the amorphous to the crystalline state in pure tellurium films and to give a preliminary interpretation of the results.

Amorphous tellurium films were prepared by vacuum deposition at approximately 10^{-5} Torr onto cooled copper foil substrates. The evaporation source consisted of tellurium powder enriched to 50% ^{125}Te contained in a shallow vitreous carbon crucible which was joule heated. A fine tungsten screen covered the source material to prevent splattering. A special sample holder was used to keep the film cool during deposition and while transferring the sample to the Mössbauer apparatus. A 2.5 cm diameter copper plug with 0.01 cm thick and 1.6 cm diameter central window was threaded into a copper block through which liquid nitrogen was circulated. The tellurium was

deposited on the surface of the plug and the gamma rays transmitted through the thin copper window which served the dual purpose of keeping the film cold and of filtering the Te K x-rays emitted from the Mössbauer source. Visual observation of the film during deposition gave a good indication of the film quality. Polycrystalline films up to several microns thick were also prepared by deposition on room temperature substrates. Films deposited on substrates held at about 100 K produced amorphous films which could not be formed thicker than about 2 microns. During the deposition, thicker films tended to partially crystallize, pucker at the center of the substrate, and eventually peel or flake off altogether. Thin amorphous films \lesssim 1 micron thick could be crystallized in situ by warming to room temperature, but those appreciably greater than 1 micron in thickness failed to adhere to the substrate when crystallized.

The Mössbauer spectra were obtained using an ^{125}I in Cu source for the 35.5 keV gamma ray corresponding to the $\frac{3}{2} \rightarrow \frac{1}{2}$ recoilless-resonant transition in ^{125}Te . The Te K x-rays were filtered by the 0.1 mm Cu substrate while the 7 keV Cu x-rays produced in the Cu matrix source were filtered by a 0.5 mm Al foil. The gammas were counted by gating on the 6 keV escape peak from a 2 atm Xe/CO₂ proportional counter. The source and absorber were both maintained at the temperature of liquid nitrogen. The spectrometer consists of a constant acceleration electromechanical velocity transducer of conventional design together with a multichannel analyzer operated in the normalized mode for collecting and

displaying the data (6). The resulting spectra were computer analyzed by a least-squares fit to the data points using a modified program originally due to Chrisman and Tumolillo (7).

Fig. 1 shows the spectra of the same sample ~ 1 micron thick before and after crystallization. Both spectra were taken with source and absorber at ~ 80 K. The spectrum of the amorphous sample could not be fit by the computer in any consistent fashion. Thicker amorphous samples giving slightly better spectra were fit with, however, fairly large errors in the fitting parameters. The solid line shown for the crystalline sample spectrum corresponds to the least squares computer fit. The spectra of the amorphous samples show little detail on account of a low recoil-free fraction and also possibly because of a non-unique quadrupole splitting. The thicker crystalline films deposited on substrates at room temperature gave Mössbauer parameters identical to those of polycrystalline powder samples within experimental error except for an asymmetry in the intensity of the quadrupole doublet components which we have verified as being due to a preferred crystal orientation in the film.

For the polycrystalline films, the quadrupole splitting (QS) is found to be 7.0 ± 0.2 mm/sec averaged over four separate measurements. The amorphous films have a QS of 8.5 ± 0.5 mm/sec averaged over three measurements. Both values of QS are for the films at 80 K.

These results indicate that there is a significant

increase in the QS as well as a large decrease of the recoil-free fraction in the spectrum of the amorphous film compared with the crystalline film. The spectra of the amorphous films are not sufficiently resolved to determine whether there is an isomer shift or any other subtle difference between the two phases.

The increase in the QS in the amorphous phase is similar to that seen in the Te rich glass $\text{Te}_{81}\text{Ge}_{15}\text{As}_4$ by Hafemeister and de Waard ⁽⁴⁾ and can be understood in terms of a change in the local structure surrounding a majority of the tellurium atoms. The electric field gradient (EFG) at the Te nucleus which is responsible for the QS is principally due to the covalent bonding electrons. According to a recent study by Boolchand, et al. ⁽⁸⁾, the ^{125}Te Mössbauer QS has been found to correlate linearly with the inverse cube of the covalent bond lengths between Te and the isoelectronic crystalline hosts S, Se and Te. This correlation is phenomenological, but can be qualitatively justified in terms of the various known contributions to the EFG at the Te nucleus. The covalent bond length in trigonal Te at room temperature is 2.84 \AA ⁽⁹⁾. Using the relationship between QS and bond length found by Boolchand, et al. ⁽⁸⁾, we find the dominant bond length in amorphous Te to be $2.75 \pm 0.04 \text{ \AA}$. Here we have assumed that there is a unique (or dominant) QS which is due to the covalently bonded atoms and have neglected the small effect of temperature on the bond length. The poorly resolved spectra and broad lines of the amorphous sample clearly indicate that the results are quali-

tative, and further, that the QS is probably not really unique. This is to be expected if the long chains are broken and disordered since Te atoms at the ends of the chains will have dangling bonds and would not experience the same EFG as their interior neighbors. Recent measurements of the radial distribution function obtained by electron diffraction experiments on amorphous Te films give a peak at 2.79 Å for the first nearest neighbor distance (10).

The lower recoil-free fraction (rff) in the amorphous state can be interpreted in terms of the changes in the lattice structure. There is little pertinent information available in the literature at this time. Raman scattering on crystalline and amorphous tellurium (11,12), reveals marked differences in the phonon density of states between the two phases. Pine and Dresselhaus, in their Fig. 4 (11) give the phonon density of states for a particular lattice model of crystalline tellurium. The corresponding density of states for amorphous tellurium cannot be easily obtained from the Raman spectra. The Raman spectrum of amorphous Te (Ref. 12, Fig. 1) shows an increased scattering at low energies ($20 \leq \bar{\nu} \leq 100 \text{ cm}^{-1}$) plus a shift to higher energy and a broadening of the sharp crystalline peaks at about 120 cm^{-1} and 140 cm^{-1} . Without knowing the details involved in converting the Raman scattering data into a phonon density of states, it would be difficult to make a precise statement concerning the change expected in the

Mössbauer rff. The structure which appears in both phases at energies greater than 100 cm^{-1} cannot greatly affect the Mössbauer rff since the classical recoil energy of the Mössbauer gamma photon, $E_R = 5.4 \times 10^{-3} \text{ eV}$, is less than half the energy corresponding to the excitation of a phonon at 100 cm^{-1} ($12.4 \times 10^{-3} \text{ eV}$). An enhanced density of low energy phonon states in the amorphous phase qualitatively is indicative of a lower rff which agrees with our observation.

Our results are consistent with a model of amorphous tellurium in which the long spiral chains of the crystalline state are broken, leaving a disordered array of shortened chains having dangling bonds at their ends. The remaining covalent bonds are slightly shortened and the phonon density of states is changed so as to increase $N(\bar{\nu})$ for $\bar{\nu} \lesssim 100 \text{ cm}^{-1}$.

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Figure Caption

FIG. 1 Mössbauer absorption spectra of the same tellurium film, 50% enriched ^{125}Te and $\sim 1 \mu$ thick, as deposited (amorphous, above) and after annealing for a few minutes at room temperature (crystalline, below). The source was ^{125}I in Cu and in both spectra the source and absorber were at 80 K.

