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Mössbauer studies in thin films of FeTe

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Room-temperature Mössbauer spectra of thin films of FeTe deposited on amorphous substrates were taken. It is seen that the film structure is basically similar to the bulk; the observed variations in the Mössbauer parameters reflect on the thickness dependence of dangling-bond configuration in the films. It is seen that the films show a tendency towards oriented growth. An attempt to investigate the influence of the substrate on the film structure was made.

I. INTRODUCTION

Structural properties of thin films have been a subject of extensive studies in the recent years because of their multifarious application in fields such as integrated circuitry and microelectronics. The major techniques used for such studies have been electron microscopy, and x-ray, electron, and neutron diffractions. The diffraction studies, however, fail to give any idea about the degree of covalency of bonds, the coordination number, phonon frequencies, and the degree of order. Radial distribution functions sometimes lead to ambiguous information[1] regarding coordination number.

The methods stated above being inadequate, it is desirable to explore the possibility of supplementing the existing thin-film data by other suitable methods. Mössbauer spectroscopy is one such tool which has not been fully exploited so far.

Some Mössbauer studies on thin films have been reported in the literature. Studies in thin films of iron[2] have indicated that the hyperfine field is maintained in films up to thicknesses as low as 10 Å. Boolchand *et al.*[3] made Mössbauer studies of Ge_xTe_{1-x} alloy films and proposed a structural model which was later modified by other workers.[4] Corciovei *et al.*[5] suggested the appearance of the Goldanskii-Karyagin effect in noncubic thin films. Valenta *et al.*[6] considered the problem of spatial distribution of spontaneous magnetization in thin films using the molecular-field approximation and the Green's-function technique. The present work was initiated with the aim to study the variation of Mössbauer parameters with film thickness so as to derive information regarding the structure and nature of bonds.

No structural studies have so far been reported on thin films of FeTe. In bulk form the Fe-Te system near 1:1 stoichiometry has been studied with the help of various methods[7] including Mössbauer spectroscopy. The β phase which exists in a narrow range of concentration near $Fe_{1.11}Te$ was studied by Suwalski *et al.*[8] and Fano *et al.*[9] Suwalski *et al.* observed a single quadrupole doublet in the spectrum of $Fe_{1.11}Te$. Fano *et al.* fitted two quadrupole doublets to the data on $FeTe_{0.95}$ and attributed them to two nonequivalent sites of iron. There is a certain disagreement regarding the phase also at 1:1 stoichiometric ratio. While Chiba *et al.*[10] reported the existence of two phases, Hansen[7] reported a single phase having hexagonal structure. Albanese *et al.*[11] studied FeTe using the ^{125}Te isotope and observed a quadrupole doublet. They attributed the asymmetry of the lines to preferential orientation of monocrystals. In the present study, the Mössbauer spectrum of bulk FeTe was taken not only to provide a reference for thin films, but also to see if the existing discrepancies in the literature can be reduced.

II. EXPERIMENTAL DETAILS

Bulk FeTe was obtained from Alfa Products, USA and was characterized by comparing the *d* lines of the observed x-ray diffraction patterns with the standard values. Thin films were deposited on Mylar substrates using the flash evaporation technique which is suitable in cases like the present one, where the vapor pressures of constituents forming the evaporant compound differ substantially. Hot tantalum boats were used for evaporation and the film thickness was monitored using a quartz-crystal oscillator. To have sufficient ^{57}Fe content in the films a few stacks of films having the desired thickness were deposited by introducing thin layers of SiO between two consecutive layers of the deposited material. For characterization, some films deposited on freshly cleaved NaCl single-crystal slices were studied by electron diffraction. The observed *d* values agreed well with those of the bulk and no lines other than those corresponding to FeTe were present. Mössbauer spectra were taken with the help of a 400-multichannel analyzer coupled to a constant acceleration drive. The γ-ray source was ^{57}Co in Pd matrix.

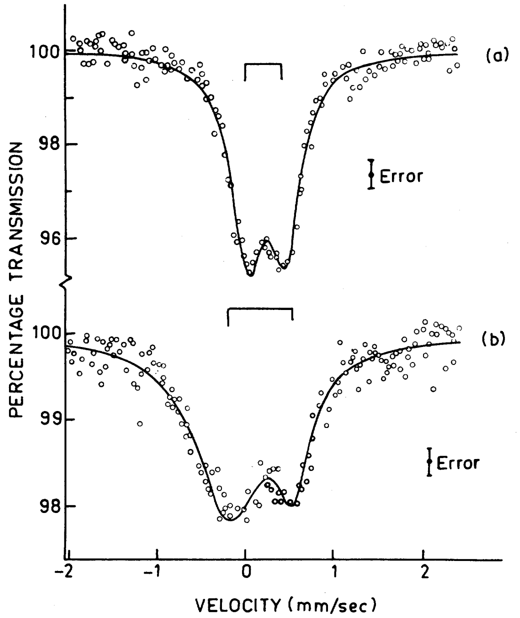

FIG. 1. Room-temperature Mössbauer spectra of (a) FeTe bulk, and (b) 80 Å FeTe film on Mylar substrate.

III. RESULTS AND DISCUSSION

The computer-fit spectrum of bulk FeTe [Fig. 1(a)] showed two lines which we attribute to a quadrupole doublet. The parameters of this doublet are given in Table I. The possibility that these lines correspond to different charge states of iron was ruled out on the basis of electronegativity[12] considerations and on the basis of the existence of a noncubic symmetry that is known to exist at the Fe site in the hexagonal structure of FeTe.[7] The observed isomer-shift (IS) value of 0.224 ± 0.022 mm/sec suggested a highly covalent $3d^24s4p^3$ hybridized state of the Fe^{2+} ion which is in agreement with the low-spin configuration[13] of iron in the octahedral field of FeTe. The quadrupole-splitting (QS) value of 0.428 ± 0.022 mm/sec also suggests a high degree of covalency. In light of Suwalski's work,[8] the ligand contribution to the electric field gradient (EFG) was calculated using the point-charge model, taking into account the strong covalency of the Fe-Te bond. The calculated EFG gave a QS value of 0.422 mm/sec. This being in good agreement with the observed QS suggests that the main contribution to EFG comes from ligands.

Mössbauer spectra of films of thickness 80, 180, 700, 2000, and 4000 Å were taken. Each spectrum showed two lines. Figure 1(b) shows a typical spectrum which corresponds to 80 Å thickness. The two lines though broadened could not be resolved further. Unless there is an appreciable change in the coordination number or the basic crystal structure in the films, a material which shows one noncubic site in bulk would not show two cubic sites in films. The *d* lines observed in the diffraction study of the bulk and of the thin films did not indicate any such changes. Each of the two-line spectra observed in case of thin films was therefore attributed to a quadrupole doublet whose parameters are given in Table I.

Figure 2 indicates a decrease in the IS values with decreasing film thickness for range below 1000 Å. This implies an increase in the *s*-electron density at the iron site. As indicated earlier, in FeTe iron is in the Fe^{2+} state with $3d^24s4p^3$ hybridization and has a low spin configuration in which all the six *d* electrons are paired into three shells. The two empty $3d$ orbitals, along with one $4s$ and three $4p$ empty orbitals, form six hybridized orbitals which are covalently bound to the ligands. If one of the bonds is broken, an orbital gets dehybridized so that the electrons distributed in the $3d^24s4p^3$ hybridized shells partly come back to the two $4s$ shells corresponding to the $3d^64s^2$ structure of iron. This leads to an increase in the *s*-electron density at the iron nucleus.

The decrease in IS values observed at lower thicknesses thus indicates unsatisfied bond structure having some missing bonds (also referred to as dangling bonds). The low mobility of ions deposited on a substrate at room temperature leads to unsatisfied bonds and incomplete crystal struc-

TABLE I. Mössbauer parameters of freshly deposited FeTe films on amorphous substrates.

Thickness (Å)	IS (mm/sec)	QS (mm/sec)	W_1/W_2	W_1 (mm/sec)	A_1/A_2
80	0.17 ± 0.023	0.738 ± 0.028	1.98 ± 0.40	0.994 ± 0.040	2.92 ± 0.29
180	0.214 ± 0.024	0.562 ± 0.028	1.23 ± 0.20	0.616 ± 0.034	1.39 ± 0.17
730	0.229 ± 0.018	0.500 ± 0.023	1.62 ± 0.30	0.611 ± 0.027	1.90 ± 0.19
2000	0.234 ± 0.016	0.468 ± 0.022	1.49 ± 0.20	0.535 ± 0.020	1.75 ± 0.16
4000	0.24 ± 0.014	0.507 ± 0.019	1.30 ± 0.18	0.526 ± 0.016	1.62 ± 0.11
Bulk	0.224 ± 0.018	0.428 ± 0.022	1.04 ± 0.20	0.454 ± 0.020	1.0 ± 0.10

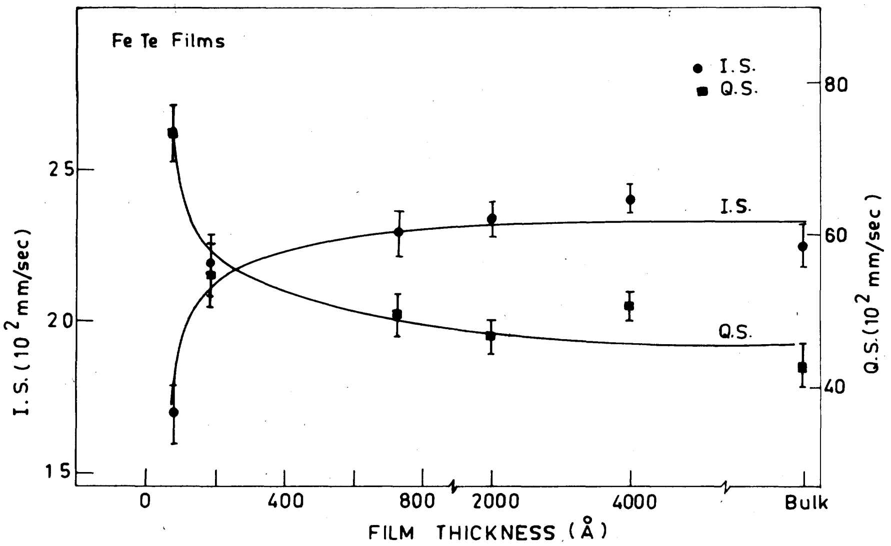

FIG. 2. Variations of IS and QS values with film thickness.

tures in the initial stages of the film growth. As the deposition process continues, some of the ions reaching the substrate go and fill the gaps left in the initial stages of film formation and complete some of the missing bonds, thus lowering the dangling-bond density. Further, the near uniform IS value above 1000-Å thickness being equal to the bulk value suggests that the change in dangling-bond density above this thickness is small. A study of films deposited on heated substrates would throw light on how substrate temperature influences the critical thickness above which dangling bonds disappear and the films behave like bulk.

The QS values as seen from Fig. 2 show an increase with decrease in film thickness, indicating a greater degree of crystal distortion. An increase in the ionic character of bonds could give a similar variation in the QS values. An increase in the ionic character however, would result in a simultaneous increase in the IS values. Since in the present study we observed an opposite variation, namely, a decrease in the IS values, the second possibility is ruled out. The greater degree of crystal distortion indicated in thin films is in concurrence with the presence of dangling bonds and the incomplete crystal structures. The almost constant value of QS above 1000 Å indicates an absence of dangling bonds above this thickness in conformity with the IS results.

As mentioned earlier, the Mössbauer lines for

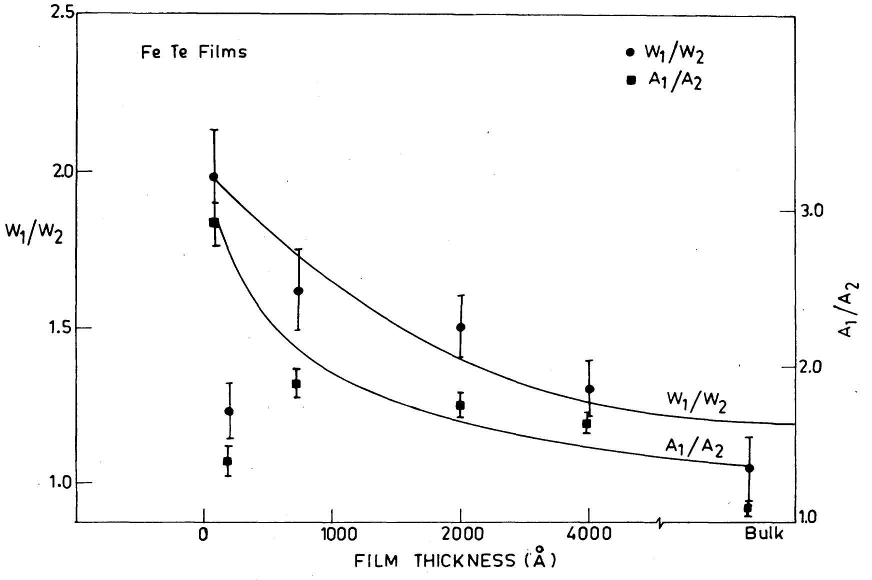

FIG. 3. Variations of W_1/W_2 and A_1/A_2 with film thickness.

the FeTe thin films in general were broadened in comparison to those of the bulk. From Table I it is clear that the first line at the lower velocity is broader than the second one for all film thicknesses; the width asymmetry (W_1/W_2) decreases with increasing film thickness (Fig. 3). In general, line broadening in Mössbauer spectra suggests the presence of relaxation effects and/or structural disorder. In the present study onset of magnetic relaxation in thin films of paramagnetic FeTe is ruled out since (i) no magnetic dilution was incorporated during film formation, (ii) the spectra for both bulk and thin films were taken at room temperature, and (iii) no change in the spatial separation of Fe^{2+}-Fe^{2+} ions has been indicated in either the diffraction patterns or by the QS and the IS values. Thermal relaxation is expected to be observed only near the melting point of the sample.

Structural disorder leads to different environments at the various iron sites. If the IS and QS values corresponding to these environments differ to an extent too small to be resolved into separate lines, the superposition of the spectra from the different sites would give broadened lines. Furthermore, if the IS and the QS values vary in a specific way, one of the lines can be more broadened than the other.[14] Such an asymmetry in the broadening has been observed by Preston *et al.*[15] in the spectra of some disordered alloys. Since in the present study the presence of any significant relaxation is not likely, the observed asymmetry in line widths is due to the presence of structural disorders. Film of a particular thickness would have some variation in the dangling-bond configuration from one iron site to another nonequivalent iron site. This results in different IS and QS values for different nonequivalent iron sites.

Furthermore, since the presence of dangling bonds affects the QS and IS parameters in an opposite fashion, the bond configuration that leads to a higher QS value corresponds to a lower IS value. The result of this correlation between the QS and IS variations is a cummulative broadening of the first line (at lower velocity) of the quadrupole doublet. The second line remains almost unaffected since the shift in its position due to any change in QS value is in the opposite direction to the shift due to the corresponding change in IS value.

As discussed in Ref. 14, it is easy to see that the observed correlation between the IS and the QS variations (with dangling-bond density) would lead to greater broadening of the first line (at lower velocity) than of the second line. The width of the first line which is a measure of the degree of disorder in the film is seen to decrease with increasing thickness (see Table I). This indicates a lower disorder at higher thicknesses and is in concurrence with the observed QS and IS variations with film thickness.

The areas under the two peaks were seen to be unequal, indicating the presence of the Goldanskii effect and/or of preferential orientation of the monocrystals.

The magnitude of the observed asymmetry is too large to be due to the Goldanskii effect alone (especially in the case of the film having 80 Å thickness) and reflects on the presence of preferential orientation of crystallites in the films. The existence of oriented growth or fiber structure in films at all stages and for all types of film growths has been reported.[16] On amorphous substrates, the existence of fiber structure has been reported for low thicknesses.[16] In the present study, the area asymmetry and hence the degree of preferential orientation was found to decrease with increasing film thickness (Fig. 3).

At 80 Å, where the area asymmetry is observed to be maximum, the film is known to be discontinuous and in the form of islands scattered on the substrate.[16] Wade and Silcox,[17] on the basis of their small-angle electron-scattering experiments on low-thickness films of Pd, Ni, and permalloy, reported that these islands are like columnar crystallites which tend to be aligned in specific directions; they observed a considerable regularity in the distribution of these crystallites in the film plane. Our observation is indicative of the presence of a similar oriented structure.

In the present study, the observed decrease in the area asymmetry with increasing thickness indicates that during coalescence of islands, orientation present in the initial stages becomes lesser. A rough estimate of the variation of area asymmetry with the relative angle between the γ-ray direction and the axis of orientation was made by studying the 4000-Å film at an inclination of 45°. A definite change in the A_1/A_2 value (from 1.30 ± 0.18 for 0° to 0.97 ± 0.22 for 45°) supports the presence of fiber texture in the films.

A. Aging effects

It was observed that when the 80 Å film was studied after being kept in a desiccator for a few months, the area asymmetry disappears. No other significant changes in the spectral parameters were observed. Since the film was covered with a sufficiently thick layer of SiO and was kept at room temperature throughout, the external influences such as atmospheric contamination and annealing conditions could not have caused the change in the area asymmetry. This indicates the existence of a highly oriented metastable state in freshly deposited films of 80-Å thickness. The absence of aging effects on other Mössbauer parameters indicates that the degree of crystal distortion and the nature of bonds remain unaffected; the dangling-bond configurations also do not change.

B. Substrate influence

Mössbauer spectra of films deposited using aluminium foils as substrate were very different from the spectra corresponding to films on mylar substrates. Each of the spectra in the former case showed a single line which though broadened could not be split and this indicates the absence of any appreciable EFG at the iron sites. The cubic symmetry observed in these films reflects on the influence of the substrate on the structure of the deposited film. Since aluminum is a cubic fcc lattice, our observations indicate that the structure of the substrate is maintained in films. IS values for these films (0.061 ± 0.015 mm/sec for the 500-Å film and 0.026 ± 0.022 mm/sec for the 1000-Å film) were different from the values for films deposited on amorphous substrates. This suggests that the substrate influences not only the crystal structure but also the nature of the bonds.

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