JOURNAL OF MATERIALS SCIENCE 17 (1982) 2061–2066

The microhardness of $Cd_xHg_{1-x}Te$

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The Vickers hardness of $Cd_xHg_{1-x}Te$ alloys has been measured as a function of composition, from $x = 0$ to $x = 0.6$, and at $x = 1.0$, at 300 K in darkness, on single crystal or large grain polycrystalline samples. Microhardness values ranged from 26 kg mm^{-2} for HgTe, rising to ~ 70 kg mm^{-2} for $x \simeq 0.6$, and dropping to about 50 kg mm^{-2} for CdTe, and the dependence on composition indicates that a maximum must occur somewhere in the range $0.6 < x < 1.0$. The hardness–composition curve is discussed in terms of possible models of solid solution hardening in this system, and the results are compared with the behaviour in metallic systems.

1. Introduction

The II–VI binary compounds CdTe and HgTe form a continuous series of solid solutions, of general formula $Cd_xHg_{1-x}Te$, which crystallize in the sphalerite structure. The band-gap of these ternary alloys varies continuously from −0.15 eV for HgTe ($x = 0$) to 1.5 eV for CdTe ($x = 1$) at 300 K. Material with compositions close to $x = 0.2$ and $x = 0.3$ are important as a narrow band-gap semiconductor for use in intrinsic infra-red detectors operating, respectively, in the 8 to 14 μm and 3 to 5 μm wavelength ranges at 77 K and 180 K.

In contrast to the common elemental (Group IV) and III–V compound semiconductors such and Si and GaAs, which deform plastically only at elevated temperatures (several hundred degrees Centigrade), $Cd_xHg_{1-x}Te$ is known to exhibit macroscopic plastic behaviour even below room temperature (Baranskii *et al.* [1]). In view of the well-established influence of dislocations and plastic deformation on the electrical characteristics of semiconductors [2] it is of interest to crystal growers and device manufacturers alike to quantify this unusual mechanical behaviour. However, only very few attempts have been made to do so. Because large, perfect single crystals of $Cd_xHg_{1-x}Te$ are not available, only very few experiments on its macroscopic plastic behaviour have been reported (Baranskii *et al.* [1], Cole [3]). Rather, the nature of the bulk-grown material makes microhardness a more favourable technique.

In III–V pseudo-binary semiconductor alloy systems, measurements of microhardness against composition have been found useful in investigating the homogeneity of the material (Goryunova *et al.* [4]). Since the hardness of most materials is a function of the yield stress, hardness data also provide a good general impression of the mechanical properties. However, the small size of the indent and the complex nature of the stress field around it makes the test very sensitive to surface preparation and anisotropy of elastic and plastic properties. Care is necessary to eliminate errors due to these effects.

Koman and Pashovskii [5] and Kurilo *et al.* [6] have measured, as a function of temperature, the microhardness of $Cd_xHg_{1-x}Te$ ($x \simeq 0.1$ to 0.25; grown by various methods), HgTe and CdTe. Sharma *et al.* [7] studied the variation of hardness of cast $Cd_xHg_{1-x}Te$ with composition across the quasi-binary section, measured at room temperature. However, whilst fair agreement is found between the results of these authors for HgTe and CdTe, considerable variations occur in measurements on the ternary compound. Indeed, Koman and Pashovskii [5] found a difference of 50% in the hardness of $Cd_xHg_{1-x}Te$ of very similar compositions grown by different methods.

In view of these inconsistencies, the present work was undertaken to obtain a large number of measurements of the hardness of $Cd_xHg_{1-x}Te$ over a wide composition range, using well-characterized material. The few results of Sharma *et al.*

0022–2461/82/072061–06$03.22/0

[7] were obtained with quenched ingots, which would be expected to have a dendritic "cored" structure (Barlett *et al.* [8]) and would be highly inhomogeneous on a microscopic scale. The composition was assumed, nevertheless, to be uniform and equal to that of the original melt. In contrast, in the present study, a large number of measurements are made on well-characterized homogeneous crystals, and the composition is measured very close to the hardness indentations.

2. Experimental procedure

2.1. Material

Slices of HgTe, cut variously on {1 0 0} and {1 1 1} orientation from single crystal grown by the travelling heater method [9], were supplied by CNRS, Meudon, France. $Cd_xHg_{1-x}Te$ was obtained in the form of slices cut from ingots grown by the Bridgman method (Barlett *et al.* [10]). These ingots were not single crystals, so the slices, cut perpendicular to the growth axis, contained sections of a number of grains. The crystallographic orientation of the surface planes of these grains was not measured in this study. CdTe slices of various crystallographic orientations were obtained from ingots grown by solvent evaporation [11] by colleagues at RSRE, Malvern.

2.2. Preparation of samples

Each slice was lapped flat on carborundum (600) grit, cleaned in methanol, and then free polished for two minutes in 5% bromine–methanol (a 5 vol% solution of bromine in methanol) to remove surface work damage. The HgTe and $Cd_xHg_{1-x}Te$ slices were then etched in a solution consisting of $12\,cm^3\,HNO_3$, $5\,cm^3\,HCl$, $1\,cm^3\,CH_3COOH$, $18\,cm^3\,H_2O$, $0.02\,cm^3\,Br_2$ (Polisar *et al.* [12]) which is a dislocation etchant for these materials (Brown and Willoughby [13], Cole [3]). Etching times were; 20 sec for HgTe {1 1 1}; 30 to 45 sec for $Cd_xHg_{1-x}Te$ and 3 min for HgTe {1 0 0}. Major grain boundaries, sub-grain boundaries and individual etch-pits were revealed, and a typical result is shown in Fig. 1. Major grains rarely exceeded 1 cm diameter, and sub-grain sizes ranged from 20 to 200 μm. Between the etch pits the surface remained flat, and therefore suitable for microhardness indentation. In the case of CdTe, on the other hand, no etchant could be found which both revealed structural defects and left an otherwise flat surface. Therefore the CdTe slices were indented in the chemically-polished condition.

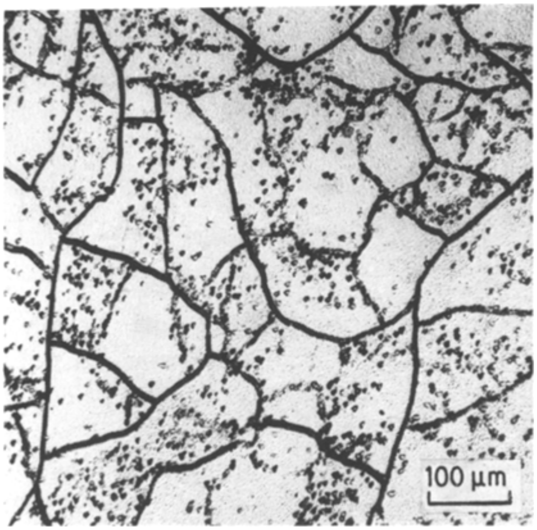

Figure 1 Microstructure of $Cd_xHg_{1-x}Te$ etched for 45 sec in Polisar etch 2.

2.3. Microhardness tests

Microhardness tests were conducted using a Vickers microsope-mounted indentor system, model M12a, applying a load of 20 g for 20 sec via a Vickers diamond pyramid. This load was sufficiently small to suppress any tendency to cracking, which can grossly affect the hardness measurements. Twelve indents were made on each slice, in three groups of four, with a rotation of about 30° between the groups. This was designed to bring out any hardness variation due to anisotropy of the plastic behaviour of the crystal, so that an average value would be obtained. (This was necessary because the crystallographic orientation of the surface differed from sample to sample.) The specimens were in darkness during the indentation process, to preclude any influence of the photoplastic effect known to exist in CdTe [14]. The indents were about 20 μm square. Measurements made on indents sited very close to sub-grain boundaries and remote from them indicated that these boundaries produce a very slight hardening effect, of perhaps 1 or 2%. Therefore, for each slice, the indentations were made within a well-etched major grain, one in each of the larger sub-grains (diameter $>100\,\mu$m), well clear of the boundaries and individual etch-pits (Fig. 2). This was not, of course, possible for the (unetched) CdTe crystals, but, as will be seen later, the scatter obtained in the results was, nevertheless, very small.

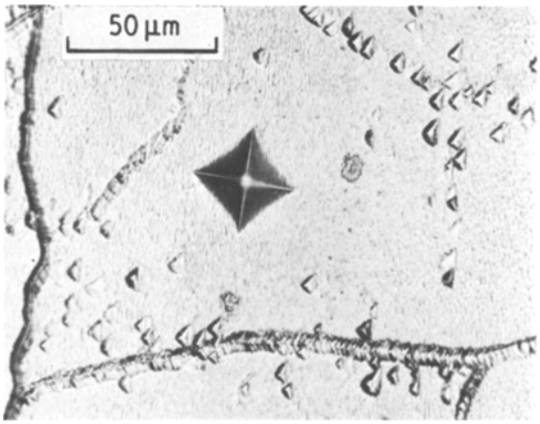

Figure 2 Typical siting of a microhardness indent within a sub-grain, well clear of the boundaries.

2.4. Composition measurement

Since the segregation coefficient in the CdTe–HgTe system is very different from 1, a considerable longitudinal compositional gradient exists in Bridgman ingots of this material, so that a range of compositions is available from a single ingot. Slices of average composition up to about $x = 0.6$ were available for this study. In the range $0.2 < x < 0.35$ the slices are roughly uniform with respect to composition, and infra-red transmission (IRT) measurements, made by colleagues at another laboratory, were used to obtain an average x-value for the whole slice. (The band-gap against composition data of Schmit [15] were used.) However, for x-values outside this range, radial variations of composition are significant [16] and an average value for the slice becomes meaningless. Therefore, in such slices, the hardness indentations were grouped together as closely as possible without interacting, and the composition was measured in their midst by electron-probe microanalysis (EPMA). 25 keV electrons were used, sampling from 1 μm^3 of the specimen. The standards were 99.999 % pure Cd and Te.

To check the compatibility of the two methods of composition measurement, samples at about $x = 0.2$ were measured by both IRT and EPMA, and excellent agreement (within 2 %) was obtained between them. Overall accuracy in measurement of x is expected to be better than 1 % (i.e. $x \pm 0.1$).

3. Results

The hardness results obtained are plotted as a function of composition in Fig. 3, along with corresponding data taken from the literature.

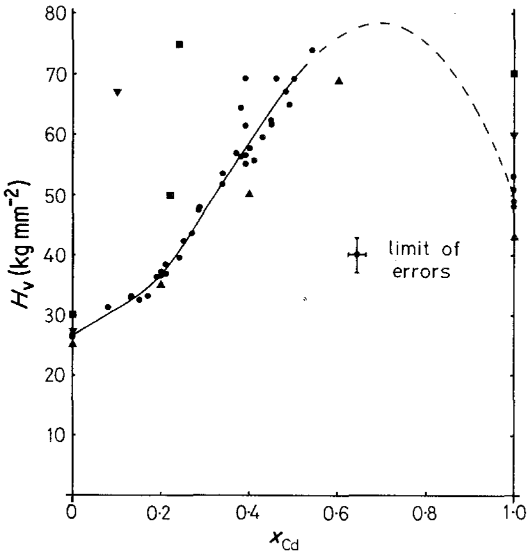

Figure 3 Vickers hardness number (H_v) of $Cd_xHg_{1-x}Te$ as a function of composition [plotted as mole fraction CdTe x_{Cd}]; ● present results; ▲ Sharma *et al.* [7]; ■ Koman and Pashovskii [5]; ▼ Kurilo *et al.* [6].

There is excellent agreement amongst all the authors on the hardness of HgTe, rather less agreement for CdTe and considerable scatter in values for the ternary compound. The present results, however, show remarkably little scatter, and lie in the midst of the literature data. They exhibit two main features.

(a) It is clear that, in the composition range investigated, addition of CdTe to HgTe to form the solid solution produces a hardening effect. Furthrmore, $Cd_xHg_{1-x}Te$, having $x > 0.3$, is harder than either HgTe or CdTe, implying that a peak must occur in the hardness–composition curve somewhere in the range $0.6 < x < 1.0$.

(b) There is a marked change in the "hardening rate", dH/dx, in the region $x \sim 0.2$. It increases from about 400 kg mm^{-2} for $x < 0.2$ to about 1100 kg mm^{-2} for $x > 0.2$. It is interesting that a similar trend is seen in the results of Sharma *et al.*

4. Discussion

The results show, that at room temperature, alloys in the $Cd_xHg_{1-x}Te$ system are very soft ($H_v <$ 70 kg mm^{-2}) compared with, for example, III–V semiconductors of similar melting point; e.g. InSb, $H_v = 220$ kg mm^{-2}, $T_{mp} = 552°$ C; InAs, $H_v =$ 430 kg mm^{-2}, $T_{mp} = 969°$ C [4] (the melting point, T_{mp}, of $Cd_xHg_{1-x}Te$ alloys lie between about 670° C for HgTe and 1094° C for CdTe). Indeed, their hardness is comparable to that of pure annealed Al ($H_v = 37\,\text{kg mm}^{-2}$ [17]). Note that this hardness, H_v, measured in this study is about 25 times the yield stress, σ_y, ($1.7\,\text{kg mm}^{-2}$ measured at 30° C. [3]) as found for other single crystals (Gerk [18]), i.e.,

$$H_v = 25\sigma_y. \qquad (1)$$

A peaked form of the hardness against composition curve is commonly observed in many binary and pseudo-bindary solid solutions series; for example in metals (e.g. Cu–Ni [19]), alkali halides (e.g. KCl–KBr [20]) and III–V compounds (e.g. $\text{In}_x\text{Ga}_{1-x}\text{Sb}$ [4]). For homogeneous solid solutions, the curve is accurately described by the empirical relation [4]:

$$H_v = (H_A - H_B)x + H_B + Kx(1-x), \qquad (2)$$

where H_A and H_B are the hardness of the pure components, and K is a positive constant. (The form of this relation has been justified theoretically for alkali halide systems by Shrivastava [20] using a theory of solid solution hardening in these materials due to Kataoka and Yamada [21]. Excellent agreement was obtained with experimental results.)

The hardness against composition curve corresponding to Equation 2 is plotted as Fig. 4. It can be seen that the present results deviate from this ideal behaviour in the region $x \sim 0.2$. Such deviations are generally taken as indicative of inhomogeneity (e.g. precipitation) in the system [4]. It might, conversely, be argued that, since the deviation occurs in the region where the method of composition measurement changed over from EPMA to IRT, the effect may be an artefact of the experimental technique. Let us look at these possibilities in turn.

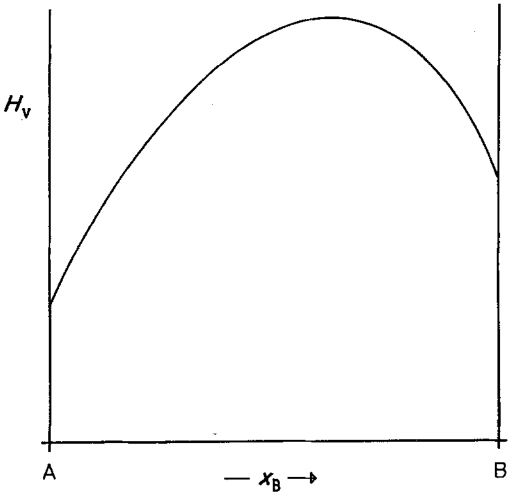

Figure 4 Form of the ideal hardness (H_v) against composition (x_B) curve for a binary solid solution, AB, corresponding to Equation 2.

(a) The scatter in the present results is small, escpecially in the composition range concerned, in spite of the fact that they were obtained from measurements on a large number of different crystals. Therefore, any precipitation effect must be systematic. However, although the extent of the solid solution outside the pseudo-binary plane is unkown, electron microscopy studies (Gillham and Farrar, [22]) (which showed Te precipitates in Te-rich material), have detected no evidence for precipitation in as-grown $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$, as long as the (Cd, Hg) to Te ratio is carefully maintained at 1 to 1, through the preparation of the starting charge. In all the crystals used in this work, this was true to within 2%.

(b) It has already been stated that EPMA and IRT measurements on the same material at compositions around $x = 0.2$ gave agreement in the x-value to within 2%. It is therefore considered that the two techniques are compatible, and unlikely to cause a deviation in the hardness–composition curve such as that observed.

It seems reasonable to say, therefore, that the observed deviation from Equation 2 is not due either to precipitation or to the change in the method of composition measurement, but may, rather, be an effect inherent to the $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ system. The similarity of the results of Sharma *et al.* (Fig. 3), in spite of the fact that their material was produced in a totally different way, is further evidence for this hypothesis. (Indeed, the good overall agreement between the present results and those of Sharma *et al.* casts doubt over certain of the measurements of Kurilo *et al.* [6] and Koman and Pashovskii [5]). [See Fig. 3]. It is interesting to note that the range in which the deviation occurs is also roughly that of the semiconductor/semi-metal transition ($x \simeq 0.1$).

In search of an explanation for these observed effects, let us consider the possible mechanisms of solid solution hardening in $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$, assuming the solution to be random (there is no documented evidence for ordering in this system).

Solid solution hardening is caused by interaction of solute atoms with the dislocations in the crystal. This can occur in a number of ways, but only the two more important mechanisms are considered here: the elastic interaction and the electrical interaction. They will be discussed in the context of $Cd_xHg_{1-x}Te$.

The elastic interaction has two components. Firstly, if the solute atom differs in size from the matrix atom it replaces, a local strain field is set up which (depending on its sign) repels or attracts the strained core of a dislocation. Secondly, if the elastic modulus is locally altered by the presence of the solute atom, work is done as a dislocation passes the site. Fleischer [23] has attempted to quantify these contributions in terms of two misfit parameters: ϵ'_b, the size misfit, and ϵ'_a, the modulus misfit. The total "elastic misfit" is then $\epsilon_T = (\epsilon'_a + \alpha \epsilon'_b)$, where α is a constant depending on the nature of the rate-controlling dislocations. While these parameters are only approximate, they are a useful guide to the magnitude of the elastic effect. A very rough calculation, using Fleischer's definitions, for $Cd_xHg_{1-x}Te$ gives $\epsilon'_b \simeq 10^{-3}$, $\epsilon'_a \simeq 10^{-2}$, so that $\epsilon_T \simeq 10^{-2}$, taking $\alpha = 3$ for screw dislocations [23] which are known to be rate-controlling in III–V compounds [24]. These are orders of magnitude down on the values found in, for example, metallic systems (e.g. Cu alloys, $\epsilon_T \simeq 1$ [23].) The initial yield stress hardening rate, $d\sigma/dx$, (obtained using Equation 1, from the experimentally determined dH/dx) expressed in terms of G, the shear modulus of HgTe, is $\sim G/1100$. This is very low compared with values for other substitutional solid solutions (e.g., $d\sigma/dx \sim G/20$ for substitutional atoms in Cu [23]), and is consistent with the small calculated elastic misfit parameters.

An electrical solute–dislocation interaction occurs if the dislocations carry a charge, and the solute atom or ion carries a different charge from the matrix atoms or ions. In the case of a Cd ion replacing an Hg ion, the slight difference in fractional ionicity, f_i, of CdTe and HgTe (0.717 and 0.65 respectively; Phillips [25]) might be expected to produce a small local charge relative to the matrix. This could interact with a dislocation line charge. [In fact, the situation is more complex than this, since the Phillips ionicity is calculated for a bulk crystal, not for an isolated ion, so we can only speculate on the relative charge on the Cd ion. Also, the dislocation line charge is likely to be a function of solute concentration (composition).] Whilst such an electrical interaction would probably be small, it may be significant, bearing in mind the tiny elastic contribution.

If we now consider the variation of electrical characteristics of the material with composition, a possible model for the anomalous behaviour in the low x range comes to light. The free carrier concentration falls with increasing x from a maximum for compositions below about $x = 0.1$ (where the band-gap is less than or equal to zero). A high concentration of free carriers would be expected to produce a screening effect which would limit the effectiveness of the electrical (Coulomb) interaction discussed above. Thus, one might expect the electrical interaction to be screened out at low x, and only the elastic contribution would be observed there. As x increases, and the free carrier concentration decreases, the screening becomes less effective, and both elastic and electrical effects are seen.

This is, clearly, a simplified approach and makes assumptions about the relative magnitudes of the elastic and electrical contributions. However, it does successfully explain the experimental observations qualitatively. Further information concerning the validity of this model might be obtained by performing experiments at different temperatures, or with electrically-active dopants, modifying the free carrier concentration as a function of solute concentration.

Finally, it must be noted that the discussion assumes that any variation in Te concentration within the solid solution is either small, or random, and thus plays an insignificant part in the hardening curve; this assumption cannot yet be tested experimentally.

5. Conclusion

The Vickers hardness of well-characterised crystals of $Cd_xHg_{1-x}Te$ alloys has been measured as a function of composition (for $0 < x < 0.6$ and $x = 1.0$) at 300 K in darkness.

(a) The values obtained (lying between 26 kg mm^{-2} for HgTe and about 70 kg mm^{-2} for $x \simeq 0.6$) are comparable with those of very soft metals (such as pure annealed Al).

(b) The hardness–composition curve must exhibit a peak somewhere in the range $0.6 < x < 1.0$. This is typical of a binary or pseudo-binary solid solution system.

(c) The hardness–composition curve deviates from the ideal solid solution behaviour in the low x region. A possible explanation for this is proposed in terms of the composition dependence of the relative magnitudes of the elastic and electrical solute–dislocation interactions.

(d) Roughly calculated values of the Fleischer elastic misfit parameters for $\mathrm{Cd}_x\mathrm{Hg}_{1-x}\mathrm{Te}$ ($\epsilon'_\mathrm{b} \simeq 10^{-3}$, $\epsilon'_\mathrm{a} \simeq 10^{-2}$) are very small compared with those found for metallic systems. This fits in with the low observed hardening rate, $\mathrm{d}\sigma/\mathrm{d}x \simeq G/1100$.

Acknowledgements

The authors are deeply indebted to colleagues at RSRE, (Malvern) and CNRS, (Meudon, Paris) for provision of the material used in this study. Thanks are due to Dr P. Capper and colleagues at Mullard, Southampton for performing the IRT measurements; and Mr E. J. Heath of the Mechanical Engineering Department, the University, Southampton, for the EPMA work. Financial support for this project from the SRC is also acknowledged.

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Received 9 November
and accepted 10 December 1981