Laser ultrasonic sensing of the melting and solidification of cadmium telluride

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Abstract

A noninvasive laser ultrasonic method has been used to investigate the melting and solidification of a (Cd,Zn)Te alloy during vertical Bridgman growth. A single zone vertical Bridgman furnace was integrated with a laser ultrasonic system and used to monitor the time-of-flight of ultrasonic pulses that propagate across an ampoule during the melting and solidification of Cd$_{0.96}$Zn$_{0.04}$Te. The measurement approach is based upon the difference in the elastic stiffness of the solid and liquid phases of Cd$_{0.96}$Zn$_{0.04}$Te (Queheillalt et al., J. Appl. Phys. 83 (1998) 4124) and its significant dependence upon temperature. This results in a reduction of the longitudinal wave ultrasonic velocity as the temperature was increased (from ambient temperature) followed by a $\sim$45% decrease upon melting. The laser ultrasonic sensor provided a robust in-situ method for monitoring the melting and solidification of Cd$_{0.96}$Zn$_{0.04}$Te. The data indicated that the melting was slow and that solidification was accompanied by a 10–15°C undercooling.


0. Introduction

The now well documented difficulties associated with the growth of premium quality Cd$_{1-x}$Zn$_x$Te (with $y = 0.04$) alloys [1] have stimulated an interest in the development of ultrasonic sensor technologies to noninvasively monitor growth conditions during vertical Bridgman (VB) solidification. Noninvasive in-situ sensors are needed to implement closed loop feedback control of crystal growth processes. Here, we explore an optical approach (laser ultrasonics) for monitoring temperature changes and liquid–solid transformations in a CdTe system. The principle underlying this sensing methodology is the strong temperature dependence of the ultrasonic velocity in the solid and liquid phases, and the large increase in the longitudinal wave velocity upon solidification [2]. These effects arise from temperature dependent softening of elastic stiffness constants and the accompanying change in density associated with thermal expansion.

Early attempts to apply an ultrasonic approach to solidification sensing sought to exploit the acoustic impedance difference across a solid–liquid interface by detecting ultrasonic reflections...
from the interface. A pulse-echo approach was investigated by Parker et al. [3] for Si, by Jen et al. [4] and Carter et al. [5] for Ge. For both of these semiconductors, good solid and liquid elastic constant and density (hence ultrasonic velocity) data existed in the literature [6–10] and the measured time-of-flight of signals reflected from the solid–liquid interface was used to estimate the interface position as solidification progressed. However, the large usually poorly characterized axial temperature gradient combined with a significant temperature dependent velocity introduced uncertainties in mapping time-of-flight data into the interface’s axial position, and little information was inferred about interfacial curvature by this method. An alternative approach sought to exploit the ultrasonic delay when ultrasonic rays were transmitted through the solid and liquid phase. Norton et al. [11] and Mauer et al. [12] have reported measurement of the time-of-flight for rays transmitted through a solid–liquid interface during the controlled solidification of an aluminum alloy. Using the predictions of a heat flow model, they were able to construct an interface geometry model and used a simple ray tracing code in conjunction with the temperature dependent elastic stiffness and density data, to compute the time-of-flight values for a fan beam set of rays propagating from arrays of source and receiver points on the boundary of the body. A nonlinear least-squares reconstruction technique was then used to fit for the unknown coefficients of the interface geometry model and thus robustly reconstruct the interface position and shape from a small transmission ray path data set.

Laser based ultrasonic techniques utilize a pulsed infrared laser to generate elastic waves with ultrasonic frequencies and a laser interferometer to detect the surface displacements associated with their arrival at a surface [13]. This noncontact ultrasonic measurement approach can be utilized at elevated temperatures where conventional piezoelectric transducers fail. It can also function in high or low pressure environments where the ultrasonic couplants used with contact ultrasonic methods may cause difficulties, and it possesses a broad bandwidth [14,15]. First proposed in the late 1970s, laser ultrasonic approaches have since been used for physical property measurements such as elastic modulus determination, [16–20] microstructural characterization, [17,21–32] and measurement of the crystallographic texture of bulk solids [33–37]. These methods have also been used for thickness gauging, [38–41] and elastic property determination [42–46] of thin films and nano-structured materials [47–52]. More recently, this technique is beginning to be used for in-situ measurement of internal temperature profiles, [53,54] monitoring of solid–solid phase changes, [54,55–57] consolidation kinetics of ZnO ceramics, [58] thickness variations of SiN films manufactured by chemical vapor deposition (CVD) [59] and for silicon wafer temperature measurement during rapid thermal processing [60].

Here, a laser based ultrasonic transmission approach has been investigated to monitor the melting and solidification of a Cd$_{0.96}$Zn$_{0.04}$Te alloy. The sensors development is based upon the recognition that the ultrasonic velocity (and the elastic stiffness constants and density that control it) of the solid and liquid phases of (Cd,Zn)Te alloys are temperature dependent and an abrupt increase of the longitudinal wave velocity occurs upon solidification. As a result, the time-of-flight of rays diametrically traversing the region of solidification exhibit a $\sim$100% increase upon melting because the ultrasonic velocity ($v$) and the time-of-flight ($t$) are directly related ($v = l/t$, where $l$ is the propagation distance). In addition, the experimentally measured longitudinal wave times-of-flight were compared with simulated time-of-flight predictions for quasi-isotropic wave velocities evaluated from the polycrystalline average of the single crystal elastic stiffness constants.

1. Experimental procedure

1.1. Sample preparation

Cd$_{0.96}$Zn$_{0.04}$Te ingots were supplied by Johnson Matthey Electronics (Spokane, WA). The polycrystalline ingot used was initially grown from the melt using a commercial 17-zone vertical Bridgman growth furnace. This resulted in a polycrystalline ingot with a coarse grained microstructure possessing a linear density typically less than 5 grain
diameters across the ingots diametral plane. The material consisted of precompounded infrared focal plane array (IRFPA) substrate purity polycrystalline equatomic CdTe to which Zn and Te was added to reach the target zinc concentration of 4at% ±1%. The ingots were encapsulated in 30 mm ID (36 mm OD) quartz ampoules with quartz plugs (to fill in the free volume) and sealed under 10⁻⁶ Torr with a very small free volume to inhibit the vaporization of Cd during heating. The free volume was less than 2% of the ingots total volume.

1.2. Laser ultrasonic sensor

The ultrasonic time-of-flight between precisely positioned source and receiver points were measured using a laser ultrasonic system (see Ref. [2] for details). Briefly, a ~10 ns duration Q-switched Nd : YAG laser pulse of 1.064-μm wavelength was used as the ultrasonic source. The energy per pulse was ~10 mJ and the roughly Gaussian beam of the multimode pulse was focused to an approximate circular spot of 1 mm diameter. Thus, the source power density was ~100 MW/cm². This was chosen to keep the generation laser power density below the threshold for cracking the quartz ampoule. The quartz ampoule was transparent to the infrared laser pulse. As a result, absorption occurred at the CdTe-quartz interface and provided a constrained surface that enhanced the ultrasonic signal strength [13].

A Mach–Zehnder heterodyne laser interferometer was used for ultrasonic detection. It responded to the sample’s out-of-plane (normal) surface displacement associated with the ultrasonic wavefront arrivals at the receiver point. It was powered by a 5 mW HeNe laser which produced a continuous Gaussian beam of 632.8 nm wavelength focused to a circular spot ~100 μm in diameter. The signal from the interferometer was bandpass filtered between 10 kHz and 10 MHz and recorded with a precision digital oscilloscope at a 2 ns sampling interval using 8-bit analog-to-digital conversion. To improve the signal-to-noise ratio, each waveform used for a time-of-flight measurement was the average of ~10 pulses collected at a pulse repetition rate of 20 Hz. A fast photodiode identified the origination time for the ultrasonic signals.

1.3. Integrated growth furnace

The ingots were heated with a single zone programmable tubular furnace (1200°C max, 6 in diameter). The furnace was equipped with a temperature controller that was able to maintain the temperature to within 1°C. The Cd₀.₉₆Zn₀.₀₄Te samples were supported by an alumino–silicate machinable ceramic and quartz support tube assembly. The laser source and receiver gained access into the furnace through small (~4 mm) slits along the diametral plane of the furnace. The sample temperature was measured with two type R thermocouples affixed to the quartz growth ampoule with tungsten wire. In both cases, the thermocouples were in physical contact with the outer surface of the quartz support tube assembly. Variations of the temperature in the region of the sample were better than ±2°C. Scanning was accomplished using mirrors attached to translation stages which were controlled using stepper motors. The screw driven translation stages had a movement resolution of 1.27 μm/step with a repeatability of 1.175 μm per 5.08 mm of linear travel. Fig.1 shows a schematic illustration of the experimental configuration.

2. Polycrystalline elastic properties

The single crystal elastic stiffness constants (C₁₁, C₁₂ and C₄₄) for solid and the adiabatic bulk modulus (K₈) for liquid Cd₀.₉₆Zn₀.₀₄Te have been
previously investigated [2]. They were evaluated from simple inversion techniques of the temperature dependent ultrasonic velocity obtained in primary \( <100>, <110> \) and \( <111> \) orientations and the temperature dependence of the density in both the solid and liquid phases. The elastic stiffness constants exhibited a monotonically decreasing function with increasing temperature in both the solid and liquid phases.

However, CdTe and its alloys rarely solidify as a single crystal. Therefore, methods for averaging the single crystal elastic stiffness constants \((C_{11}, C_{12}, C_{44}\) for cubic materials\) to obtain effective values for polycrystalline elastic moduli have been used to predict the ultrasonic behavior of the polycrystalline material. The isotropic polycrystalline elastic constants include Young’s modulus \((E)\), the bulk modulus \((K)\), the shear modulus \((G)\), Lame’s constants \((\lambda, \mu)\) and Poisson’s ratio \((\nu)\). Several authors [61–65] have proposed methods to estimate the polycrystalline moduli and several thorough reviews have been published by Ledbetter [66], Hearmon [67] and Hashin [68].

The elastic properties of polycrystalline bodies depend on the macroscopic behavior of a polycrystalline body’s individual single crystals (crystallites or grains). In principle, the averaging problem can be solved by considering simultaneously the elastic equilibrium equations for each grain together with the boundary conditions at grain interfaces; in practice, this approach poses insurmountable problems [69].

Most averaging methods assume, either explicitly or implicitly, certain conditions in the polycrystalline body [69]:

- The number of grains composing the body is sufficiently large.
- Grains are randomly oriented; that is preferred orientations are absent.
- Grains sizes do not vary so much that a few orientations contribute dominantly.
- Grains are not so small that their crystallinility is lost.
- Elastic stiffnesses are homogeneous within a grain and between crystallites.
- Grain boundaries per se contribute nothing to the body’s elastic properties.

For materials with a cubic symmetry, the averaging problem consists of reducing the three independent elastic stiffness coefficients to two independent constants that describe completely the elastic behavior of quasi-isotropic solids (i.e. those solids whose properties are anisotropic locally but isotropic macroscopically) [69]. The bulk modulus is a scalar invariant of the elastic stiffness tensor and is represented by

\[
K = \frac{1}{3}(C_{11} + 2C_{12}).
\]

It is assumed that the polycrystal and single crystal bulk moduli are equal and therefore the grain boundaries contribute nothing to the polycrystalline elastic properties.

The problem remains, to determine a second polycrystalline elastic stiffness constant. The second constant cannot be chosen uniquely. Generally, Young’s modulus and the shear modulus are often calculated. The most straightforward of the averaged quantities are the Voigt \((E_V\) and \(G_V\), homogeneous strain) [61,62] and the Reuss \((E_R\) and \(G_R\), homogeneous stress) [63] averages given by

\[
E_R = \frac{5C_{44}(C_{11} - C_{12})(C_{11} + 2C_{12})}{C_{11}^2 + C_{11}C_{12} - 2C_{12}^2 + 3C_{44}C_{11} + C_{44}C_{12}},
\]

\[
G_R = \frac{5C_{44}(C_{11} - C_{12})}{4C_{44} + 3(C_{11} - C_{12})},
\]

\[
E_V = \frac{(C_{11} - C_{12} + 3C_{44})(C_{11} + 2C_{12})}{2C_{11} + 3C_{12} + C_{44}},
\]

\[
G_V = \frac{C_{11} - C_{12} + 3C_{44}}{5}.
\]

Hill [70] states the \((E_V\) and \(E_R\)) and \((G_V\) and \(G_R\)) are upper and lower bounds for the polycrystalline moduli obtained from the single crystal elastic stiffness constants and suggests two approximations:

\[
E_{VR-a} = \frac{1}{2}(E_V + E_R),
\]

\[
E_{VR-g} = \sqrt{E_V E_R},
\]

where \(E_{VR-a}\) and \(E_{VR-g}\) represent the arithmetic and geometric averages. The same arithmetic and geometric averaging can be applied to the shear
modulus \((G_{VR}/C_0a)\) and \((G_{VR}/C_0g)\):

\[
G_{VR-a} = \frac{1}{2} (G_V + G_R), \tag{8}
\]

\[
G_{VR-g} = \sqrt{G_V G_R}. \tag{9}
\]

Now, the polycrystalline elastic moduli can be calculated from the single crystal elastic stiffness constants for solid \(Cd_{0.96}Zn_{0.04}Te\). The calculated temperature dependent polycrystalline elastic stiffness moduli for Young’s and the shear moduli (Eqs. (2)–(9)) are shown in Fig. 2. In Fig. 2, the arithmetic and geometric means of the Voigt and Reuss models are sufficiently equivalent that only the arithmetic mean is shown. Table 1 shows polynomial fits for the temperature dependence of the polycrystalline elastic moduli of solid \(Cd_{0.96}Zn_{0.04}Te\).

### Table 1

<table>
<thead>
<tr>
<th>Elastic moduli</th>
<th>Temperature dependent (GPa) (T = ^\circ\text{C})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(K)</td>
<td>(42.905 \pm 7.304 \times 10^{-3}\ T - 3.249 \times 10^{-6}\ T^2)</td>
</tr>
<tr>
<td>(E)</td>
<td>(39.669 \pm 5.481 \times 10^{-2}\ T - 3.231 \times 10^{-6}\ T^2)</td>
</tr>
<tr>
<td>(G)</td>
<td>(14.745 \pm 1.985 \times 10^{-3}\ T - 1.204 \times 10^{-6}\ T^2)</td>
</tr>
</tbody>
</table>

3. **Quasi-isotropic wave propagation**

The propagation of high frequency elastic waves (ultrasound) in isotropic polycrystalline bodies is directly related to the (dynamic) elastic moduli of the body. In the long wavelength limit, the longitudinal and shear wave velocities can be expressed in terms of the low frequency limit (static) elastic constants and the density [71]. The thermal expansion characteristics of \(Cd_{0.96}Zn_{0.04}Te\) have been previously evaluated [2] and not reported here. The longitudinal \((v_l)\) and shear \((v_s)\) wave velocities were computed from well known relationships

\[
v_l = \sqrt{\frac{E}{\rho (1 + \nu)(1 - 2\nu)}} \tag{10}
\]

\[
v_s = \sqrt{\frac{E}{\rho 2(1 + \nu)}} = \sqrt{\frac{G}{\rho}} \tag{11}
\]

where \(E\) is Young’s modulus, \(G\) is the shear modulus, \(\rho\) is the density and Poisson’s ratio \((\nu)\) can be expressed as \(\nu = E/2G - 1\) and the data of Table 1. The calculated temperature dependent quasi-isotropic longitudinal and shear wave velocities (Eqs. (10)–(11)) are shown in Fig. 3. Table 2 shows polynomial fits for the temperature dependence of the quasi-isotropic wave velocities of solid \(Cd_{0.96}Zn_{0.04}Te\). In addition, the temperature dependent longitudinal wave velocity for liquid \(Cd_{0.96}Zn_{0.04}Te\) is also shown in Table 2.

![Fig. 2. Temperature dependence of the Voigt and Reuss polycrystalline elastic moduli for solid \(Cd_{0.96}Zn_{0.04}Te\).](image1)

![Fig. 3. Temperature dependence quasi-isotropic wave velocities (polycrystalline average) for solid \(Cd_{0.96}Zn_{0.04}Te\).](image2)
4. Results

The laser ultrasonic sensors response has been evaluated for two sensor configurations. In one case the growth furnace was held stationary, while the sensor recorded data for the longitudinal wave time-of-flight during melting and solidification. In a second type of experiment, the sensor’s response was monitored while the molten ingot was directionally solidified through the sensor’s region of interrogation.

4.1. Stationary furnace

4.1.1. Heating

The longitudinal wave time-of-flight measured during heating is shown in Fig. 4(a) as a function of process cycle time. The ingot was heated at a rate of 5°C/min to 1050°C, then 1°C/min to 1140°C and held for 15 min, Fig. 4(b). Also shown in Fig. 4(a) is the simulated quasi-isotropic longitudinal wave time-of-flight calculated from the polycrystalline averaged moduli. The simulated data corresponds to the arrival time-of-flight of a quasi-isotropic longitudinal wave at the sensor’s plane of interrogation using the data in Table 2 and the reference thermocouple temperature. The experimental data show a gradual increase in the time-of-flight as the ingot was heated and a discontinuous (∼100%) increase near the melting temperature indicated by the thermocouple. This discontinuous increase in the longitudinal wave time-of-flight indicates the beginning of melting. The deviation between the experimental and simulated time-of-flight near the melting point indicate that a 10–15°C superheating was necessary for the ultrasonic velocity to equilibrate to the quiescent reference velocity. It should also be noted, Fig. 4(a), that the longitudinal wave time-of-flight in the solid phase fell below the simulated data for the quasi-isotropic polycrystalline average wave velocity. This arises from the initial coarse grain size of the ingot (only 3–5 grains diameters). The limited number of grain orientations resulted in a sample that was not truly isotropic.

4.1.2. Cooling

The longitudinal wave time-of-flight measured during cooling is shown in Fig. 5(a) as a function of process cycle time. The ingot was cooled from 1140°C at 1°C/min to 1050°C, then 5°C/min to room temperature, Fig. 5(b). Also shown in Fig. 5(a) is the simulated quasi-isotropic longitudinal wave time-of-flight. Again, the simulated time-of-flight was calculated from the isotropic polycrystalline elastic constants at the temperature measured by the reference thermocouple. The experimental data show a gradual decrease of the time-of-flight as the sample was cooled and exhibited a discontinuous decrease (∼50%
decrease) at a temperature of 1085°C. The discontinuous decrease in the longitudinal wave time-of-flight is indicative of the solidification of the ingot. However, a significant amount of supercooling was observed with the ultrasonic sensor, revealing that solidification occurred between 1090°C and 1085°C. Once the ingot solidified, the time-of-flight compared well with that predicted by the isotropic polycrystalline elastic moduli (unlike during the heating cycle). The grain size after solidification was comparable to the initial diameter. However, the average grain orientation sampled by the ultrasonic ray path during solidification was obviously different.

4.2. Directional solidification

The ultrasonic technique was used to monitor the directional solidification of Cd_{0.96}Zn_{0.04}Te as the furnace was translated at a rate of 1.67 mm/min (i.e. 100 mm/h). During the furnace translation segment, the temperature of the single zone furnace was held constant at 1140°C and the insulation zone at the bottom of the furnace provided the necessary cooling to promote directional solidification.

The longitudinal wave times-of-flight measured during the heating and the soak segments of the process cycle are shown in Fig. 6(a). The ingot was heated at a rate of 10°C/min up to 1090°C, then 1°C/min up to 1140°C, held for 60 min to equilibrate at which point the furnace translation was begun, Fig. 6(b). Fig. 6(a) also shows the simulated data for the quasi-isotropic longitudinal wave time-of-flight determined from the reference thermocouple. The data show a gradual increase in the time-of-flight as the ingot was heated, a discontinuous increase near the melting point indicating the beginning of the melting process followed by another gradual increase in the time-of-flight.

After the ingot was allowed to equilibrate at 1140°C for 60 min the furnace translation was begun. The longitudinal wave times-of-flight measured during the soak and furnace translation segment of the process cycle are shown in Fig. 7.
Fig. 7 shows a uniform time-of-flight during the isothermal soak, a gradual decrease followed by an abrupt decrease (~50%) in the time-of-flight. The gradual decrease was due to a decrease in the melt’s temperature as the insulation zone approached the sensors region. After the insulation zone passed the sensor, the liquid–solid interface propagated through the sensors plane of interrogation and the time-of-flight abruptly decreased indicating the passage of the liquid–solid interface. Fig. 8 shows the measured and deduced temperature in the plane of the sensor during the soak and growth portion of the process cycle. The data show good agreement for measurement taken in the liquid state and some scatter in the solid state. This is attributed to the anisotropic nature of the solidifying ingot.

4.3. Summary of observations

During the melting–solidification experiments, the longitudinal wave time-of-flight data exhibited a gradual increase as the ingot was heated and a discontinuous increase near the melting point. This discontinuous increase in the longitudinal wave time-of-flight indicated the beginning of the melting process for the Cd_{0.96}Zn_{0.04}Te alloy. The data indicated slow melting characteristics as the alloy was not fully molten until the reference thermocouple reached a temperature of ~1115°C. Cadmium telluride possesses a low thermal conductivity ($k \approx 1 \times 10^{-2}$ W/cm K) and high heat capacity ($C_p \approx 150$ J/g K) [72,73]. This, coupled with a low thermal gradient resulted in a small heat flux and slow melting. The measured data also exhibited a gradual decrease in the time-of-flight as the sample was cooled and a discontinuous decrease at a temperature of about 1085°C. The discontinuous decrease in the longitudinal wave indicated ingot solidification. However, the temperature of the ingot was cooled well below the melting point before solidification was observed with the ultrasonic sensor, indicating that solidification occurred between 1090°C and 1085°C.

During directional solidification, the laser ultrasonic data exhibited a gradual increase in the time-of-flight as the ingot was heated, a discontinuous increase near the melting point followed by another gradual increase indicating the ingot began melting at ~1100°C and was not fully molten until the temperature reached 1120°C. During the soak and furnace translation portion of the process cycle, the sensor indicated a relatively constant time-of-flight followed by an abrupt decrease indicating the solid–liquid interface passed through the sensor region. The time-of-flight in the liquid state was constant up to ~252 min (Fig. 7) at which point it began to gradually decrease until ~260 min. This gradual decrease was attributed to a decrease in the melt’s temperature as the insulation zone approached the sensor. As the insulation zone passed the sensor the sensor and the longitudinal wave time-of-flight
decreased abruptly indicating the passage of the liquid–solid interface. Again, the deviation between the sensors data and the simulated data has been attributed to the low thermal conductivity, high heat capacity of CdTe alloys in addition to constitutional supercooling effects.

5. Discussion

The melting behavior of CdTe follows a solid semiconductor → liquid semiconductor transition, i.e. its electrical conductivity increases with temperature. The early work of Glazov [10] suggested that a considerable amount of the covalent contribution of the cohesive energy is retained in the melt and a three-dimensional arrangement of the associated tetrahedra are retained in the superheated melt. As the superheating is increased, these tetrahedra are dissociated into two-dimensional associated (rings and chains) molecules and separate atoms. This behavior has been experimentally examined by investigating the superheating/supercooling behavior of CdTe by differential thermal analysis (DTA) and direct temperature measurement at the tip of a growth ampoule [74–77]. It was shown that at small values of superheating (<10°C), no supercooling was observed, where at values higher than 10°C, supercoolings up to 20–30°C occurred. This behavior is indicative of the observance of a structural transition in the molten state. These associated complexes in the melt (tetrahedrons, chains and rings) are likely to reduce the free energy for nucleation and promote the phase transition near thermodynamic equilibrium. On the other hand, at higher superheating levels, the thermal destruction of the associated complexes takes place and a higher driving force (supercooling) is required for solid nucleation.

Recent measurements of the electrical conductivity during heating and cooling have been used to characterize the superheating-supercooling behavior of CdTe and (Cd,Zn)Te alloys. The work of Shcherbak [78,79] and Choi and Wadley [80,81] indicated that the electrical conductivity of CdTe and its solid solution alloys undergo a discontinuous increase by an order of magnitude during melting and remains semiconducting in the liquid state (i.e. its electrical conductivity increases with temperature). These experiments confirm the superheating/supercooling behavior observed by differential thermal analysis (DTA) and direct temperature measurement at the tip of the growth ampoule. The ultrasonic measurements reported here indicated that significant superheating was necessary to fully melt the ingot (melting had begun at ~1100°C and was not fully complete until the temperature reached ~1120°C). In addition, a significant amount of supercooling (up to 15°C) was observed with the laser ultrasonic sensor. This appears to be a result of the combination of low thermal conductivity and high heat capacity of CdTe alloys. In addition, Singh et al. [82] have used an ultrasonic technique to investigate the temperature dependence of the ultrasonic velocity for molten Cd_xTe_{1-x} alloys (where 0 < x < 1 in 0.1 increments). Their data indicated that the adiabatic compressibility of stoichiometric CdTe exhibited the largest temperature dependence and observed degree of supercooling. Their work speculates that the large temperature dependence of the ultrasonic velocity in molten stoichiometric CdTe can be correlated to the dissociation of the retained covalent bond in the molten state with increasing temperature. This large temperature dependence of the ultrasonic velocity in molten Cd_{0.96}Zn_{0.04}Te has also been observed in Queheillalt et al. [2] and the present work.

6. Conclusions

The difference in the ultrasonic velocity of a longitudinal wave propagating in solid and liquid (Cd,Zn)Te has led to an interest in the use of ultrasonic time-of-flight measurements as a potential noninvasive sensing methodology to monitor the solid–liquid interface during vertical Bridgman crystal growth provided the temperature dependence of the ultrasonic velocities (which depend on the elastic stiffness constants and the density) for both the solid and the liquid phases are known a priori. The longitudinal and shear waves exhibited a monotonically decreasing velocity with temperature in the solid phase. When the alloy was
heated through the melting point under quasi-equilibrium conditions a $\sim$100% decrease was observed in the longitudinal wave velocity, due to the absence of the shear modulus in the liquid phase. These results suggest that the ultrasonic velocity ratio ($v_s/v_l$) between the solid and liquid phases is sufficient for the implementation of this sensing technology to monitor the liquid–solid interface during vertical Bridgman growth.

The laser ultrasonic sensor also provided a robust method for in-situ monitoring of the liquid–solid interface as it passed through the sensor during directional solidification. Therefore this laser ultrasonic approach exhibits the potential for providing critical information during the vertical Bridgman growth process. The integration of robust laser interferometers into vertical Bridgman growth furnaces may provide useful information to the crystal grower in efforts to obtain higher yields of premium quality semiconductors. It is believed that due to the fact that laser ultrasonic sensors may provide “real time” data, they offer the possibility of new sensor based process control technologies for in-situ monitoring and direct feedback control of vertical Bridgman growth technologies.

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References
