Lattice Dynamics of Laser-Heated GaAs Crystals by Means of Time-Resolved X-ray Diffraction

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Nanosecond time-resolved X-ray diffraction has been employed to study the transient lattice structure of GaAs crystals induced by laser pulse heating. The time evolution of lattice spacing changes was measured with 12 ns resolution. A direct imaging X-ray CCD system with high spatial resolution allowed for the detection of transient structural changes on the order of 5×10^{-4} Å.

1. Introduction

Processing of semiconductor materials by ultrashort laser pulses is a widespread technology. The rapid heating and cooling of crystals under short laser pulse irradiation have been of substantial research interest both from a basic science point of view and for its application to such processes as defect annealing in semiconductor circuits. Ultrashort laser pulses have been used not only to produce transient states in materials but also to obtain some indirect dynamic information on transient structures. The use of X-ray pulses is an ideal method for measuring transient structural changes in materials and for understanding the dynamics of laser matter interaction and its effect on structure.

X-ray diffraction is a widely used technique to obtain steady-state structural information on crystalline and amorphous materials. The diffracted intensity profiles (rocking curves) are highly sensitive to strain and damage distributions within the crystal lattice. However, the information regarding the transient structure and related dynamic properties of the bulk of materials is rather limited because time-resolved X-ray diffraction experimental systems have not been widely available. In recent years, however, the advances in ultrashort pulse X-ray sources have opened the possibility of observing directly the structural change in the bulk with nano- and picosecond time resolution, and even femtosecond resolution seems to be feasible.[1−3] For most X-ray diffraction studies the main requirement is monochromatic radiation and low beam divergence. In a typical experimental system, because of the lack of focusing optics for hard X-rays, only a small number of the photons generated in a narrow bandwidth are propagated in the small spatial angle needed for X-ray diffraction. Thus, single-shot experiments are difficult to perform because they would require very powerful X-ray sources. This has been achieved by the use of high-intensity synchrotron X-ray pulses.[4] However, because of possible damage to the sample, most often the data are obtained by the accumulation of many shots with less intense X-ray pulses. In this case a high repetition rate of reproducible pulses and a high degree of synchronization of the pumping pulses and X-ray probing pulses are necessary. These types of experiments are plausible when the process under investigation is reversible at a rate corresponding to the repetition rate of the X-ray pulses. Time-resolved X-ray experiments may be also performed if fresh samples can be supplied with the rate of the X-ray probing pulse. In recent years time-resolved X-ray diffraction studies have been demonstrated using short X-ray pulses produced by laser plasma, synchrotrons, and X-ray diodes.[1−3] Most of the studies of semiconductor materials using ultrafast X-ray pulses have been related to thermally induced melting and shock wave propagation using short laser pulses as pump sources and X-ray pulses as probes.[1] However, knowledge of the dynamics of the lattice deformation and the changes in the crystal structure at lower levels of excitation, before melting, and where no phase transition has taken place are also very important for the understanding of the structural dynamics of materials. Such studies help us also understand the process taking place in the rapid thermal annealing and thermal cycling of semiconductor materials.[5,6] In this process the rapid rise of temperature may create thermal gradients through the bulk of the crystal, which could lead to thermal stress and influence the annealing process. Understanding the transient lattice behavior would be also beneficial in multilayer structures, such as GaAs on Si substrates, because it will provide the data needed to improve the properties of such a composite system, to control the growth process, and to understand the mechanism of stress/strain development. Lattice distortions near the surface, which are formed during processing, are studied by means of asymmetric Bragg X-ray reflections (in this case the reflecting planes are not parallel to the crystal surface), which allows short-range penetration of the X-rays into the bulk of the crystal.[7] This technique is complementary to the time-resolved electron diffraction method used to study the transient structure of surfaces.[8]

In this paper we report nanosecond time-resolved X-ray diffraction measurements of transient lattice deformation of GaAs crystals under pulsed UV laser irradiation.

2. Experimental System

In this study we used a pump/probe setup where the laser pulse heats a sample and the X-ray pulse probes the structure of the sample with nanosecond resolution. The changes in the scattered X-ray radiation are recorded by a CCD and processed in order to derive the transient properties of the crystal lattice.

In our experiments an ArF excimer laser, operated at 300 Hz with a pulse duration of 12 ns, is used for both heating the sample and pumping the X-ray diode. Details of the operation of our laser-pumped X-ray diode in the picosecond and nanosecond regimes have been reported elsewhere,[9] and here,

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only the parameters of the diode related to this experiment are described. The X-ray diode employed a Cu anode, and characteristic Cu Kα radiation (λ = 1.54 Å) is used in the measurements. The X-ray probe pulse duration, which is determined by the pump laser pulse, was 12 ns. The X-ray beam impinging on the sample was formed by two parallel slits with variable widths that were separated by 180 mm. The sample was mounted on a four-axis Eulerian cradle in order to be accurate-oriented. The scattered X-ray radiation was recorded by a liquid nitrogen cooled 2K × 2K CCD camera (15 μm pixel). The CCD camera is made for direct X-ray imaging, and the geometrical resolution of the experimental system is about 50 μrad. The advantage of the large-area CCD detector is that it allows for the simultaneous recording of the reflected X-ray radiation from different parts of the sample. Thus, a signal from the laser interaction spot and a reference signal from another part of the sample where no laser impinges are recorded in the same exposure and at the same time.

Very high-quality single crystals of GaAs with (111) and (100) orientations were used in the measurements. GaAs is a strong absorber of the 193 nm radiation, with an absorption length shorter than 10 nm. Thus, the heating energy of the 193 nm pulse was deposited on a thin surface layer and the subsequent heating of the bulk takes place by heat diffusion. The energy of the heating UV pulse, as much as 3 mJ, was deposited on a rectangular spot of about 0.1 cm^2. We note that in our studies the maximum energy density was less than 50 mJ/cm^2, which is several times less than the melting threshold of GaAs (a 225 mJ/cm^2 melting threshold was reported for nanosecond pulses at 193 nm[10]). However, for UV pump pulse energies above 0.8 mJ a permanent visual change of the surface in the irradiated area was observed after several seconds of exposure to UV light. The geometrical size of the UV spot on the crystal was much larger than the X-ray penetration depth in the crystal; thus, one-dimensional distribution of the temperature and stress in the probed bulk of the crystal can be assumed.

In our studies the heating pulse energy density was well below the melting threshold, and therefore, no melting or evaporation of the sample takes place. In this case the temperature distribution in the crystal may be found by solving the heat conduction equation.[11] The calculated temperature distribution in a GaAs crystal heated by a UV laser pulse as a function of time is presented in Figure 1. As seen, in the first 50 ns after the laser irradiation a nonuniformly heated volume near the surface is created with a thickness of several micrometers. For time delays longer than 50 ns the temperature gradient in the crystal is less than 20 °C; however, this nonuniform temperature distribution will generate a strain inside the crystal.[12] The strain normal to the heated surface layer as a function of depth is given by

$$\Phi(z,t) = \int_{T_0}^{T(z,t)} \alpha(T)\eta(h,k,l)\,\mathrm{d}T$$

where T_0 is the temperature of the unheated part of the crystal, $\alpha(T)$ is the linear thermal expansion coefficient, $\eta(h,k,l)$ is a factor that takes into account the one-dimensional nature of the strain. For a cubic crystal, in which the surface is along the planes ((100) or (111)), this factor is given by[12]

$$\eta(1,1,1) = 3(1 + 2C_{12}/C_{11})/(1+2C_{12}/C_{11} + 4C_{44}/C_{11})$$

$$\eta(1,0,0) = 1 + 2C_{12}/C_{11}$$

In our calculations, we neglect the temperature dependence of the linear thermal expansion coefficient and the elastic constants (C_{ij}) because in the temperature range of our experiment they change by less than 2%.[6]

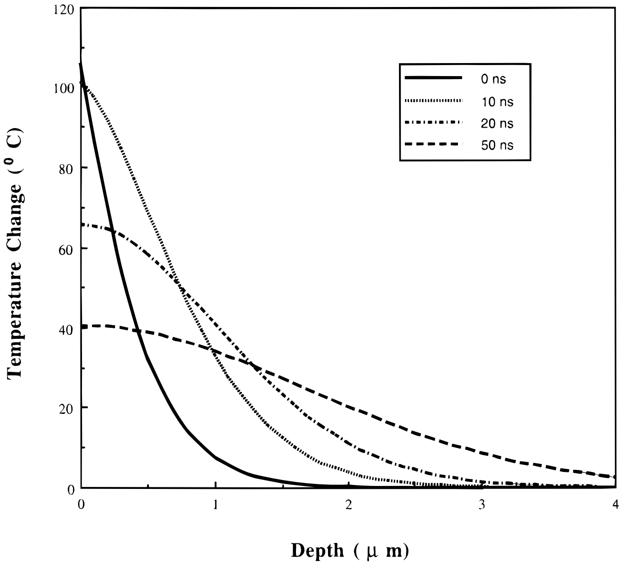

Figure 1. Calculated temperature distribution at various delay times for a GaAs crystal irradiated with a single 12 ns, 20 mJ/cm^2, 193 nm laser pulse.

For our measurements several crystals of GaAs(111) were used, all of which were cut from the same 2 in. wafer. When the crystal was held on the X-ray diffractometer by epoxy glue, because of the poor heat conduction from the crystal to the holder, a residual heating of the crystal was observed. At 300 Hz, the time between heating pulses is 3.3 ms and the heat diffusion length is about 0.4 mm. For a smaller crystal, with a 0.1 cm^3 volume, we found that at 300 Hz and 0.6 W average power delivered to the crystal in a spot of 0.1 cm^2 the residual heating was increasing the crystal temperature by about 20 °C above room temperature. Such heating of the whole crystal will result in a shift of the rocking curve even for part of the crystal not under laser illumination. When the crystal was placed on a Cu sink, no residual temperature increase away from the heated spot was observed.

3. X-ray Diffraction from Deformed Crystals

The diffraction of monochromatic X-ray radiation from a crystal is governed by Bragg's law. If small changes in the interatomic spacing of the crystal are induced, then a change in the Bragg condition will result in a shift in the diffracted angle. The relation between the angle shift $\Delta\theta$ and the lattice spacing d is given by differentiation of Bragg's law

$$\Delta d/d = -\Delta\theta/\tan\theta$$

Thus, by measurement of the angle shift information, the change in the spacing of the diffracting planes of the crystal may be obtained. In the case where the laser radiation is absorbed by a very thin layer of the surface, the temperature distribution and the associated stress in the bulk of the crystal will be nonuniform, causing a distortion in lattice spacing. When a nonuniform distribution of the lattice spacing inside the crystal is induced, the diffracted signal is composed of signals scattered over the range of angles corresponding to the lattice spacing. If the divergence of the incoming beam covers all these angles, the recorded signal will contain information about the spacing change distribution. Determination of the lattice spacing at different positions and different times is obtained from interpretation of the diffracted signal. Experimentally, the whole rocking curve may be recorded in a single shot by illuminating the crystal with a divergent beam and using a CCD detector to record the reflected X-ray radiation over the entire scattered angle.

To calculate the angle-dependent diffracted intensity, two different theoretical approaches are employed: dynamical and kinematic theory.[13] These two theories describe the X-ray diffraction from perfect and ideally imperfect crystals, respectively. The probed depth of the X-ray radiation in a perfect crystal is determined by its extinction length. Usually the extinction length is shorter than the absorption length. In a mosaic crystal the scattered radiation is effectively decoupled from the incident radiation and the X-rays are attenuated by the photoelectric absorption. In practice most crystals are somewhere between these two extremes; however, for good quality semiconductor crystals such as Si and GaAs and relatively small disturbances, the crystal may be considered perfect, and therefore, the dynamic theory is most appropriate.

Generalization of the dynamic theory to include crystals with some distortions has been developed[14,15] and applied to the X-ray diffraction from deformed crystals.[16−18] Here, we follow the approach of ref 18 in solving the dynamical equations for a slightly deformed crystal. The laser-heated crystal is divided into two parts: the disturbed region in which the strain is large enough to change the diffracted signal and the undisturbed region, which lies underneath the disturbed area. The strain in this region is so small that no significant deviation from the ideal diffraction can be observed. Therefore, the diffracted intensity can be calculated using an infinitely thick ideal crystal. This diffracted intensity then serves as the boundary condition for the disturbed part. Normally, the thickness of the disturbed region is selected to be twice the extinction length, which is defined as

$$A_{\mathrm{m}} = 2\frac{V\sqrt{|\gamma_0\gamma_h|}}{\lambda|F_h|}\left(\frac{e^2}{mc^2}\right)^{-1}$$

Here, $e^2/(mc^2)$ is the classical electron radius, λ is the X-ray wavelength, F_h is the structure factor for reflection, and V is the volume of the unit cell. Directional cosines of the incident and diffracted waves are

$$\gamma_0 = \sin(\phi + \theta)$$

$$\gamma_h = \sin(\phi - \theta)$$

Here, θ is the Bragg angle and ϕ is the inclination of the reflecting plane to surface.

To calculate the rocking curves for the laser-heated crystal, we divided the crystal into an arbitrary number of parallel layers and an average strain (temperature) was assumed for each particular layer. This kind of calculation has been shown to be accurate for steady-state X-ray diffraction.[18] Additional approximations are necessary for a crystal under transient conditions. In our case we use a simplified approach based on the physical considerations of our experiment. The calculations are carried out by slicing the input X-ray pulse into a set of micropulses with picosecond duration and then performing the corresponding calculations for every micropulse. During the passage of each micropulse the temperature distribution and related strain in the crystal are assumed to be constant but evolve with each subsequent micropulse. Thus, for every micropulse, the diffraction process may be treated as a steady-state condition.

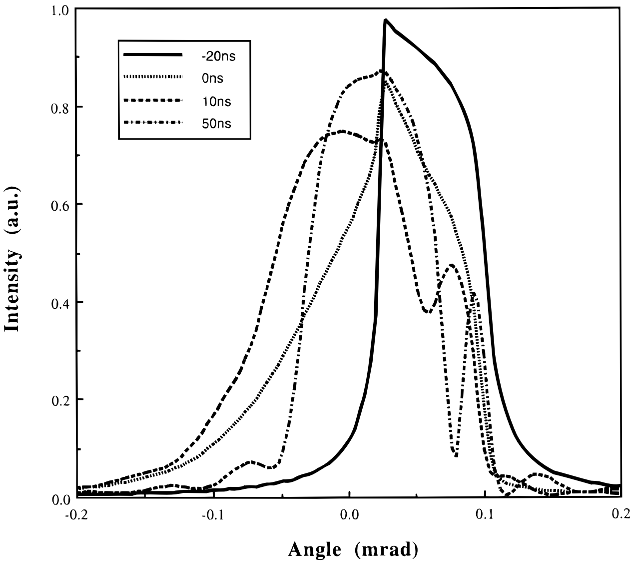

Figure 2. Dynamical diffraction theory calculation of the rocking curve at different delay times for a 12 ns X-ray pulse reflected from a heated GaAs(111) crystal.

With this approximation, we calculate first the temperature distribution $T(z,t)$ in the crystal and then the thermal strain $\Phi(z,t)$ associated with a specific $T(z,t)$. We have calculated the one-dimensional temperature distribution in the GaAs crystal by solving the conduction equation for a Gaussian pulse envelope, assuming a flat-top cross section laser beam (Figure 1). The $t = 0$ time is defined as the time when the intensity maxima of both X-ray and laser pulses overlap on the sample, and the positive delay time corresponds to the case when the probing X-ray pulse follows the heating laser pulse. We note that for such timing of the laser and X-ray pulses at zero time delay, 50% of the heating laser pulse energy is deposited on the sample.

4. Results and Discussion

We have calculated the X-ray diffracted signal for each micropulse, and then the overall diffracted X-ray signal was calculated by integrating over the entire X-ray pulse envelope to obtain the rocking curve. In Figure 2 we show the calculated rocking curves for GaAs(111) symmetric Bragg reflection at different time delays. In practice the calculated rocking curve needs to be convoluted with the instrumental broadening function. For our experimental setup the instrumental broadening function was derived from the static X-ray rocking curve and then convoluted with the calculated Bragg profiles. To obtain the whole rocking curve in a single shot, an X-ray point source is required. Therefore, the finite size of our X-ray source (determined by the slits) defines the resolution of our experiment. Although the simulated rocking curves (Figure 2) showed some shape change and broadening around zero time delay, when convoluted with the instrumental broadening function, the rocking curve became more symmetric (Figure 3). The integration of the rocking curve gives us the integrated intensity of the scattered X-ray radiation. In Figure 4 (solid line) we show the calculated integrated reflecting power as a function of the delay between the UV heating pulse and the probing X-ray pulse. As seen, the integrated reflecting power increases around zero delay. Qualitatively, we can expect such an effect because weak heating of the crystal generates layers of the crystal with slightly different lattice spacing, which consequently leads to an increase in the acceptance angle for Bragg reflection and

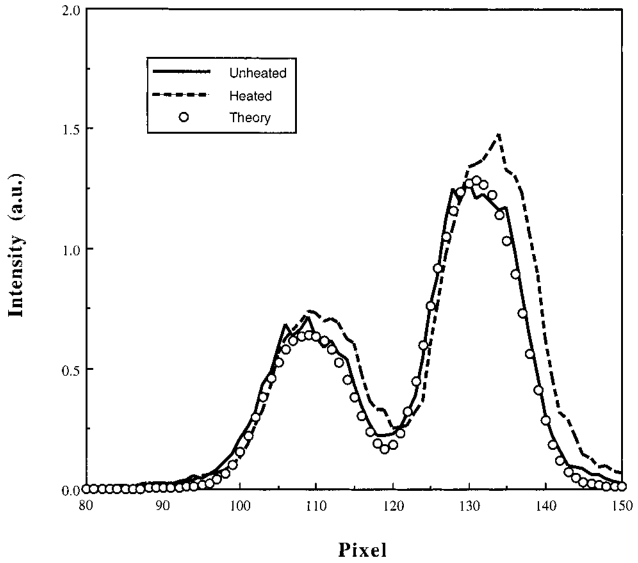

Figure 3. Experimental rocking curve for a cold and hot GaAs crystal. The delay time is 10 ns. The points are the calculated rocking curve for the cold crystal. Both Cu Kα1 (stronger) and Cu Kα2 lines are recorded. 1 pixel = 50 μrad.

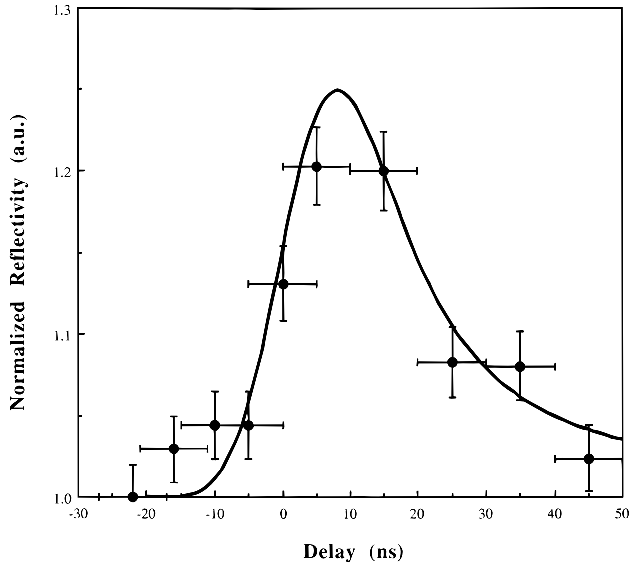

Figure 4. Calculated integrated reflectivity of laser pulse heated GaAs(111) crystal as a function of time. The points are experimental results.

therefore to an increase in the integrated reflectivity. We note that in this case the crystal is still practically perfect and that the dynamical theory is applicable. A similar increase of the integrated reflectivity from weakly curved perfect crystals was calculated for neutron scattering.[16] As the crystal is disturbed more aggressively, the crystal structure may revert to a "mosaic" one, and then an even higher increase of the integrated reflectivity is expected. We estimate using the expressions for ideally perfect and ideally mosaic crystals[13] that an increase by a factor of 5 in the reflectivity of a mosaic crystal occurs. Thus, measurements of transient reflectivity may be used as a diagnostic tool for determining if the structure of the semiconductor crystal experiences drastic changes during processing.

In our experiments we studied GaAs crystal with two orientations: symmetric Bragg diffraction from (111) planes of a GaAs(111) crystal and asymmetric (311) reflection from a GaAs (100) crystal. For these two reflections the penetration depth determined by the absorption of the X-ray radiation in the crystal differs by a factor of 4, i.e., 6 μm for the (111) reflection and 1.5 μm for the (311) reflection. The corresponding extinction lengths are the same: $A_m(111) = A_m(311) = 1$ μm. In our measurements two consecutive exposures of about 10 min each were made, the first one with UV radiation heating a selected part of the crystal and the second exposure without UV heating. Both X-ray patterns were compared to ensure that there is no change due to external effects. Since the heating takes place only at a selected spot, the rest of the pattern must be the same for both exposures, and any changes induced by the UV irradiation will show up only in the UV irradiated part of the diffracted pattern. Details of the data processing procedure have been reported earlier.[9]

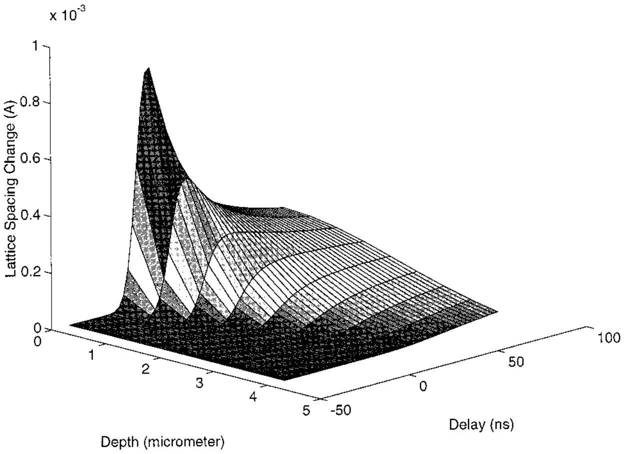

Figure 5. Lattice spacing evolution within the GaAs(111) crystal heated by a 12 ns laser pulse.

The angular width of the rocking curve for symmetric Bragg (111) reflection from a GaAs(111) single crystal using Cu Kα radiation is $\Delta\theta = 38$ μrad.[13] An angular shift of the rocking curve of this size can be achieved if the crystal temperature is increased by about 20 °C. To decrease the instrumental broadening of the rocking curve, a 0.1 mm slit was used to obtain a 2 mrad divergence of the input X-ray beam, which is necessary to cover the shift produced by the laser pulse heating. Under these conditions we detect small shape changes occurring only near the 10 ns delay time, which are due to the temperature gradient in the crystal. In Figure 3 we show the rocking curves for cold and hot crystals taken during two consecutive exposures for a 20 mJ/cm^2 heating pulse and a +10 ns delay. The shift in the rocking curve and the increase in the reflected intensity are clearly seen. In the same exposure no shift or broadening was observed in the nonheated part of the crystal. Also in this figure the theoretical rocking curve convoluted with the instrumental function for a cold crystal is presented (points). When a heating pulse is applied, the rocking curve shifts and in addition changes in its shape are observed that are due to the lattice structure deformation. The deformation is maximum near the end of the heating pulse (~12 ns). Then as the crystal cools, the curve returns to its original position. The corresponding measured integrated reflectivity is shown in Figure 4 (points). We see an increase in the integrated reflectivity in the time window of about 50 ns. Physically, this means that small deformations in the lattice structure lead to an increase in the acceptance angle, and therefore, a larger part of the incoming divergent beam will be effectively reflected. We note that the experimental points correspond to the average reflectivity over 12 ns and to the probed depth in the crystal. These data show directly the evolution of the transient structure of the crystal and its return to its original lattice spacing. This shows that the energy flux

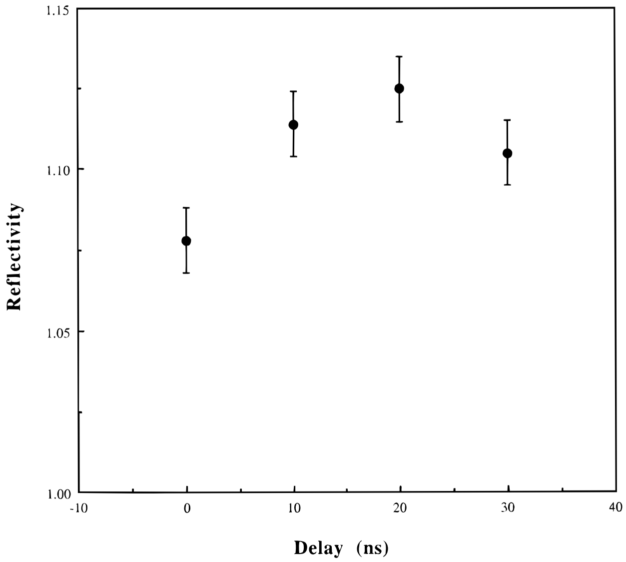

Figure 6. Experimentally measured integrated reflectivity of the asymmetric (311) reflection from a GaAs(100) crystal at various delay times heated by a 12 ns laser pulse.

supplied by the laser pulse to the crystal causes only transient structural changes and strain without a permanent effect.

When the calculated and experimental rocking curves are fitted, a profile of the lattice deformation in the crystal over a 100 ns time window was obtained. The X-ray scattering calculations were fitted to the measured data using the thermally induced lattice strain as a function of depth. Since the GaAs crystal was assumed to satisfy the dynamical theory, the penetration depth of the X-ray radiation is governed by the extinction length. Therefore, the fitting was limited to a depth of less than 1.5 μm. The temperature profile for larger depths was determined using the heat flow calculations.[11] Figure 5 shows the results of the best fitting procedure for the lattice evolution. We see that at the end of the heating pulse a maximum expansion of the lattice spacing takes place. For a heating energy of about 20 mJ/cm^2 the lattice expansion in a 1 μm layer is on the order of 8×10^{-4} Å.

Another experiment was performed using a GaAs crystal with (100) orientation because it is often used in technology. In this case the asymmetric (311) reflection was measured. The Bragg angle for (311) reflection for Cu Kα radiation is $\theta = 26.89°$. The tilt of (311) planes relative to the crystal surface (100) plane is 25.14°. Therefore, the incidence angle on the crystal was 1.75° and the reflected beam was at 52.03°. In our experiment the asymmetry ratio $b = \sin(\theta + \phi)/\sin(\theta - \phi) = 25.8$ is quite high. This is advantageous because a high asymmetry combined with the proper X-ray wavelength allows us to study the transient structure of the surface layer. For our GaAs crystal orientation and Cu Kα line, the penetration depth, as determined by the absorption, equals the penetration depth determined by the extinction, which is approximately 1 μm. This value is on the order of the heat diffusion during the 12 ns UV pulse. Time-resolved X-ray reflectivity measurements for several delays are presented in Figure 6. The reflected intensity was found to increase as was the case with the GaAs(111) crystal, showing that it was a “perfect” crystal that was not disturbed by the laser pulse sufficiently to cause permanent structural deformation, which will alter it to become “mosaic”. These measurements show that we can perform transient single-crystal topography measurements in GaAs as were done previously only for the steady-state case.[19]

5. Conclusion

The effect of short-pulse laser heating on GaAs crystals as a function of time and depth within the crystal has been studied. The transient lattice spacing associated with the change in temperature has been measured with a time resolution of 12 ns. Simple calculations using the dynamical diffraction theory agree well with the experimental data. These experiments allow us to measure directly the change in the structure and strain as a function of time, nanosecond in this case, which occur on the surface and in the bulk of a semiconductor crystal. From the histogram of the transient structure and strain evolution of a single crystal with nanosecond or picosecond resolution, we are able to record the effect of laser pulse heating on the structural integrity of the semiconductor during the irradiation process. Such information is useful also for understanding the parameters that influence the growth and processing of semiconductors.

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