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COMMENTS ON CONTAINERLESS BULK CRYSTAL GROWTH AND EPITAXY IN SPACE AND ON THEIR IMPLICATIONS REGARDING NON-CONTACT TEMPERATURE MEASUREMENTS

Klaus J. Bachmann

Department of Materials Science and Engineering
and
Department of Chemical Engineering
North Carolina State University
Raleigh, NC 27695-7907

1. Introduction

Variations in the diffusion layer thickness during the growth of single crystals from a supersaturated nutrient phase (liquid or vapor) cause striations in the concentrations of the segregating components. These striations follow the contours of the solid-nutrient interface and can be revealed for post-growth analysis by staining techniques or x-ray topography. Wafers cut perpendicular to the growth direction of a crystal, produced in a thermal geometry that results in a non-planar interface, thus exhibit a variation of the local concentrations of the segregating components (impurities, alloy components)[1]. This is particularly detrimental in applications which require uniform local properties over large distances on the wafer surface as for example in the fabrication of planar integrated circuits. Therefore, the control of the diffusion layer thickness during crystal growth is a technologically important topic. Since one of the causes for the modulation of the diffusion layer thickness is the uncontrolled variation in buoyancy driven convective flow of the nutrient, experimentation in the microgravity environment of space can contribute to the understanding and control of fluid dynamics problems in crystal growth. It is a well established component of

NASA's materials science in space program which is reviewed in more detail in the paper by Archibald Fripp in these proceedings[2].

In this paper, the aim is at containerless methods of bulk crystal growth and epitaxy which thus far are a less visible component of materials science in space efforts. In the opinion of the author, this is an anomaly which ought to be corrected, because container interactions are a major problem in earth bound materials processing, including crystal growth, and can be avoided or at least significantly reduced in space. Clearly non-contact methods of temperature measurements are essential for containerless processes. In processes requiring an ultra high vacuum they are also easier to implement in space than on the ground because of the absence of windows in the path of light beams that may change their intensity and polarization due to the clouding of the windows and strain, respectively. In view of the restrictions on the length of this presentation we focus on one example each from the areas of bulk crystal growth and epitaxy to discuss more specific requirements.

2.Containerless Bulk Crystal Growth

There exist two ways of implementing the directional solidification of contained congruently melting materials: 1. The motion of the container with the charge relative to a stationary position of the melting point isotherm (Bridgman method). 2. The motion of the position of the melting point isotherm relative to a stationary charge by slow cooling (gradient freezing method). Although appearing primitive at first glance, the gradient freezing method has been developed into a viable method for the industrial fabrication of large single crystals of III-V compounds with exceptional control of the interface shape[3]. Since this control is achieved by careful design of passive elements, and the method requires only minimum operator attention for reproducible results, it is well worth being considered in the context of remotely controlled use in space.

To relate this to containerless processing, consider a molten charge held in a stationary position in a microgravity environment by a variable levitation force, e.g. electrostatic, electromagnetic or acoustic levitation, as illustrated in figure 1. The preferred choice of the levitation method depends on the requirements regarding the surrounding atmosphere and melt composition. Providing for an appropriate axial temperature gradient and attaching a seed crystal to this melt at the point of minimum temperature on the surface of the melt, in principle, should permit one to initiate crystal growth in a controlled manner. For shaping of the crystal and the interface it may be advantageous to provide for a relative motion of the position

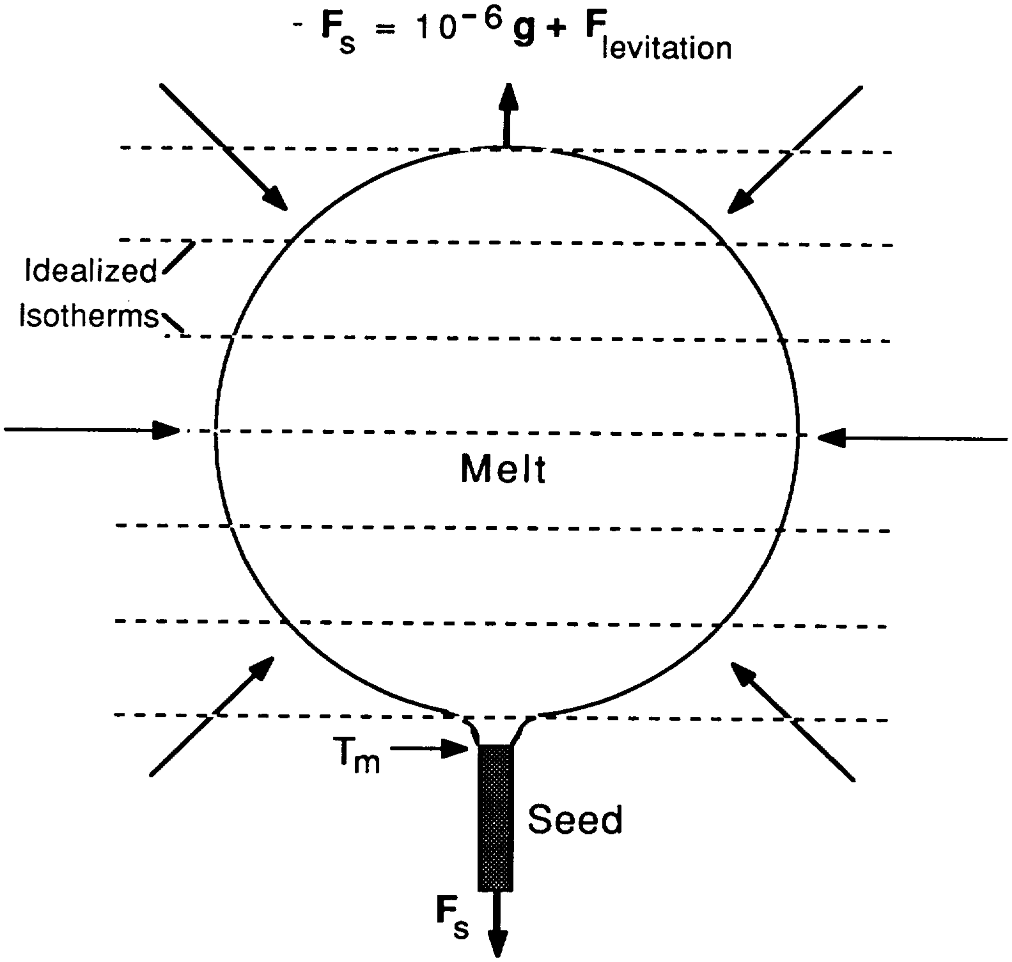

Figure 1. Schematic representation of seeded directional solidification of a melt confined to a stationary position by levitation forces

of the energy well and the seed, but not to the extent of the conditions of Czochralski pulling at 1g since slow cooling at nearly stationary position of the molten charge is the most desirable mode of crystal growth. The potential of the above method must be compared to alternative methods available on the ground, in particular float zoning and skull melting. In the opinion of the author, the above described floating drop method provides probably for greater flexibility in the control of the interface shape than the alternatives and benefits from the absence of density gradient driven convection. Therefore, it deserves evaluation by modeling and by initial experiments concerning the directional solidification of levitated melts on the ground. The method can be altered slightly for solution growth initiating nucleation by a pulse of a cold Helium jet at the point of lowest temperature on the surface of the solution followed by slow cooling.

Since the temperature distribution in the interior of the melt can be unequivocally derived from the temperature at the surface if the thermal conductivity and emissivities of the solid and liquid are known in the temperature range of interest, thermal imaging reading out a sufficient number of pixels for interface modeling will be important for the optimization of the control of the heat input into the melt, its position and the heat extraction at the seed. Fiberoptics guided sensors will be least intrusive and will permit the design of a thermal geometry that minimizes radial temperature gradients in the melt. The axial temperature gradient will depend on the material. The most interesting materials to be studied would be highly reactive compounds and elements that melt at high temperatures and that have thus container problems without solutions on earth. At present the restrictions to the power available for space experimentation make the pursuit of such crystal growth tasks unrealistic, but should not deter an evaluation of more manageable model systems, e.g. directional solidification of low melting point/low density metals and solution growth of materials that are currently in particular demand for research tasks which can be done with small crystals, but that require standards of perfection and purity unattainable by conventional methods. An example, is the growth of pure untwinned single crystals in the systems $Cu_3Ba_2YO_{7-\delta}$ where Y stands for one of the rare earth elements. Regardless of the technological potential of these compounds, in the opinion of the author, studies of their fundamental properties would benefit from access to more perfect single crystals and warrant the effort to design appropriate crystal growth methods. Of course, if these methods address general problems of crystal growth technology which are bound to remain a challenge for future advanced materials developments in general, they deserve attention irrespective of special materials needs.

3. Containerless Epitaxial Crystal Growth

In view of the increasing demands for advanced ICs incorporating optoelectronic devices, sensors and novel switching elements, e.g. based on resonant tunneling, the combination of different classes of materials on a monolithic chip is presently under intense investigation. The methods that provide for optimum resolution are molecular beam epitaxy (MBE) and (OMCVD). Currently organometallic molecular beam epitaxy (OMMBE) is being explored in several laboratories which aim at combining the best features of the two methods, i.e high uniformity (OMCVD), atomic resolution and flexibility in the control of the surface kinetics by the independent manipulation of individual ballistic source beams and UHV in-situ diagnostics (MBE). Figure 2 shows a schematic crossection of the process chamber of an OMMBE system built by the author at NCSU.

Fluid dynamics problems are absent under the conditions of these methods, but memory effects are a serious impediment to the combination of several important classes of materials in high quality heteroepitaxial structures. These memory effects are caused by the accumulation of precursor molecules and products of the surface reaction at the substrate on the walls of the vacuum chamber and pumps. If these materials have sufficient vapor pressure at operating conditions to introduce in an uncontrolled manner dopants into subsequent epilayers clearly the achievement of high quality hetrostructures is foiled. For example, the group IIB elements are

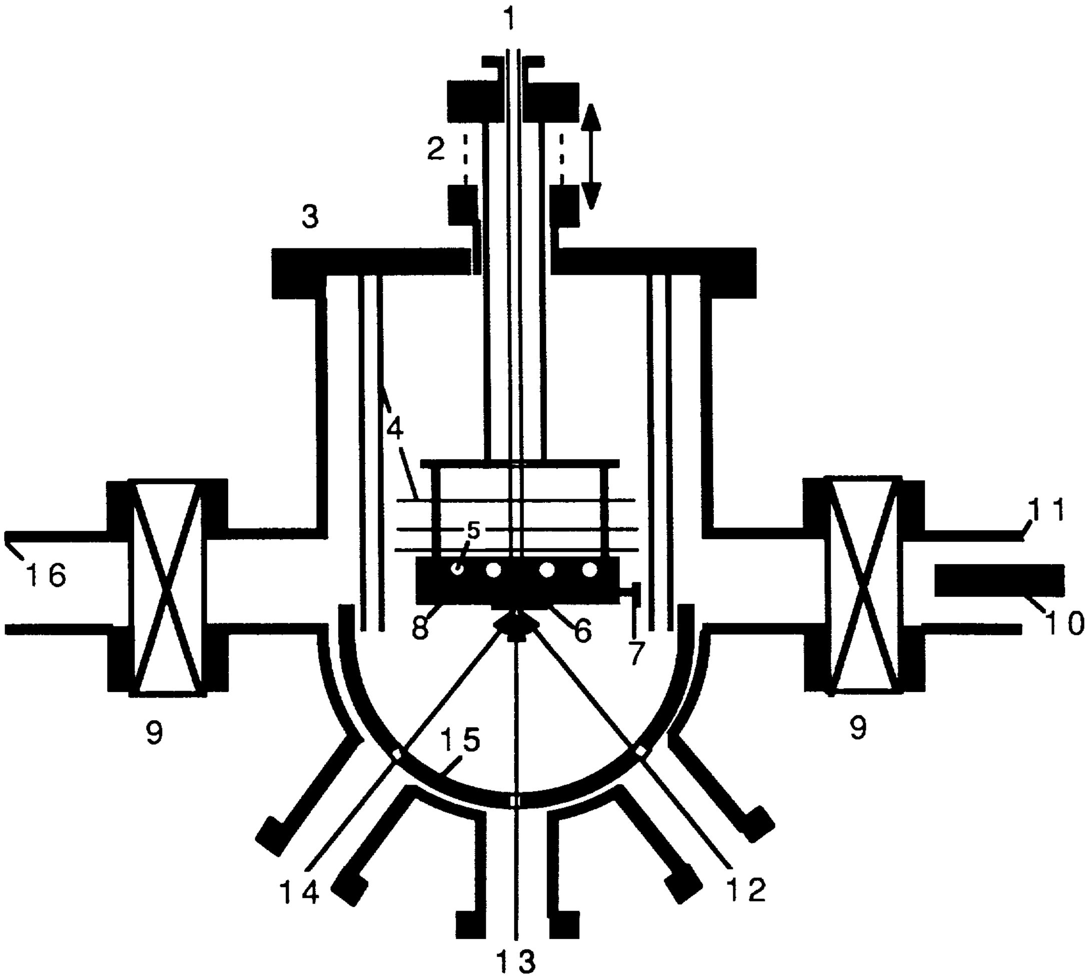

Figure 2. Schematic representation of a cross section of the process chamber of an OMMBE system[4]. 1. Thermocouple for temperature control of heaterblock 8; 2. Linear motion feedthrough; 3. Top Flange; 4. Heat shields; 5. Heater elements; 6. Substrate mounted with indium on Mo substrate carrier; 7. Key on substrate carrier engaging into pick-up tool on magnetic transfer rod 10; 9. Gate valve; 11. Tube connection to load-lock; 12.-14. Multiple OM source beam ports; 15. Cryo-shroud; 16. Tube connection to by-pass pump.

notorious in this regard making the combimation of II-VI and III-V compounds in monolithic structures extremely difficult. Similar difficulties are encountered in the growth of high resolution II-IV-V_2/III-V structures[5,6] and other classes of materials combinations for the fabrication of multilayer structures where sample transfers through gate valves prevent the maintaining reproducible growth conditions and almost certainly assure cross contamination. Therefore, the utilization of the infinite pumping rate of the space vacuum eliminating pumps and a major part of the enclosing structure of ground based UHV systems offers unique possibilities.

Non-contact temperature measurements are of particular interest in this context for the monitoring of the absolute temperature of the surface of the substrate which is a general problem in UHV. Given the drive towards low temperature processing, which is a necessity to limit reactions and interdiffusion processes at the interfaces of high resolution heterostructures, spectroscopic methods of non-contact temperature measurements become increasingly feasible. For example, photoreflectance spectroscopy is feasible in the currently preferred range of substrate temperatures, $500\text{K} \leq T \leq 800\text{K}^{7}$. It is based on the modulation of the field at the surface of a semiconductor due to the photogeneration of carriers in a modulated laser beam that strikes the surface at the same location as the unmodulated reflected probe beam of frequency ω. Structure in $\Delta R(\omega)/R(\omega)$ is observed in the vicinity of singularities in the dielectric function which occur at wave vectors **k** where $\nabla_k(E_c-E_v) = 0$. This is illustrated in figure 3 for GaAs[8]. The opportunity for utilizing the method for non-contact temperature measurements arises because the bands shift with temperature. The associated shift in the positions of the various transitions is for GaAs $10^{-4} \leq \partial\Delta E/\partial T \leq 10^{-3}$ eV/K[7,8].

The accuracy of the method is limited by the line shape which depends on the defect density in the material. Figure 4 shows the photoreflectance spectra for the E_0 transition of a series of $Cd_xMn_{1-x}Te$ crystals of different alloy composition $0 \leq x \leq 0.59$. Note the abrupt change in the line broadening at $x \geq 0.2$ which is due to a steep increase in the microtwinning and line defect density in the alloys with larger Mn concentrations. Also, note that the position of the photoreflectance signal shifts with the alloy concentration so that the error in the determination of the alloy composition adds to the error in the temperature measurement. Generally the alloy composition is well controlled in heterostructures employing semiconductor

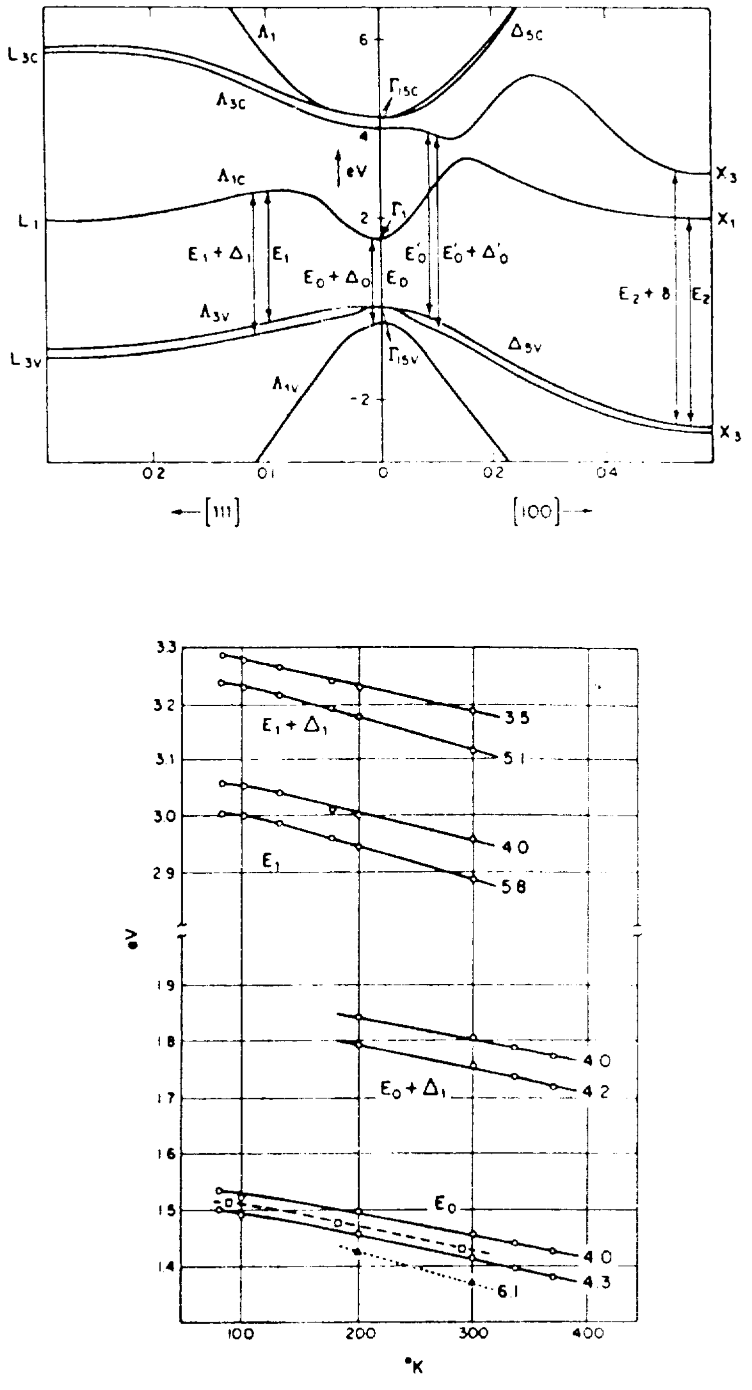

Figure 3. Positions of the interband transitions of GaAs where $\nabla_k(E_c-E_v)=0$ (top) and temperature dependence of these transitions determined by modulation spectroscopy (bottom)[8].

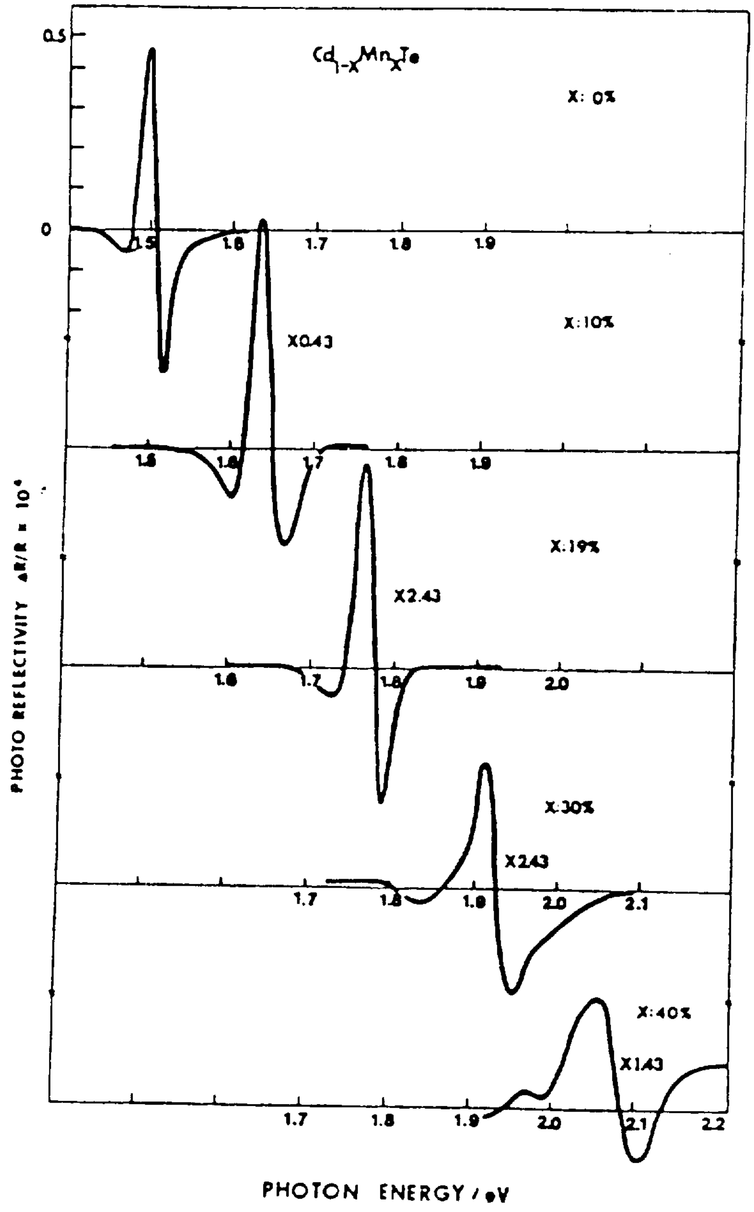

Figure 4. Photoreflectance spectra at room temperature of $Cd_{1-x}Mn_xTe$ crystals obtained at room temperature for various compositions[9]

alloys so that this error is small. It can be measured on-site without removing the wafer from the substrate stage by a variety of surface analysis methods.

An added advantage of the utilization of spectroscopic methods of non-contact temperature measurement, such as phoptoreflectance, is the simultaneous provision of valuable information on the success of the process and on radiation damage events that may occur by the collision of energetic particles with the semiconductor surface. Part of this problem is alleviated by the sweeping action of the wake shield in a space ultrahigh vacuum facility (SURF). However, light mass/high velocity particles could enter into the volume behind the wake shield and hit the substrate. This is not necessarily a problem since the growth proceeds under self annealing conditions. Both the damage and annealing could be followed by the signature provided by the photoreflectance signal. Figure 5 shows the line broadening and annealing of the radiation damage introduced into crystals of CdTe and $Cd_{1-x}Mn_xTe$ by the same dose of 3 KeV Ar^+[10,11]. Even more detailed information on the type of damage and sophisticated quality control regarding the finished heterostructures can be provided without need for retrieval of the wafer by optical spectroscopies with high spatial resolution at space ambient temperature.

In summary, there exists a need for containerless processing both with regard to bulk crystal growth and epitaxy. The space environment is unique in solving some of these problems, e.g. memory effects in the integration of different classes of materials in high resolution multilayer heterostructures by MBE or OMMBE. Spectroscopic methods of non-contact temperature measurements exist that could be developed in this context. The error in the absolute temperature measurement achieved by these techniques decreases with decreasing substrate temperature and supplements thus pyrometric measurements that are better suited for high temperature measurements. The spectroscopic methods cover a continuous range of temperatures from space ambient to a few hundred K. They provide, in addition to temperature data, valuable information on the quality of heteroepitaxial growth and on radiation damage and annealing processes without need for the retrieval of the wafer. The justification for developing these methods for use in space is predicated by the seriousness of the commitment to the development of the SURF without which no meaningful R&D program is possible.

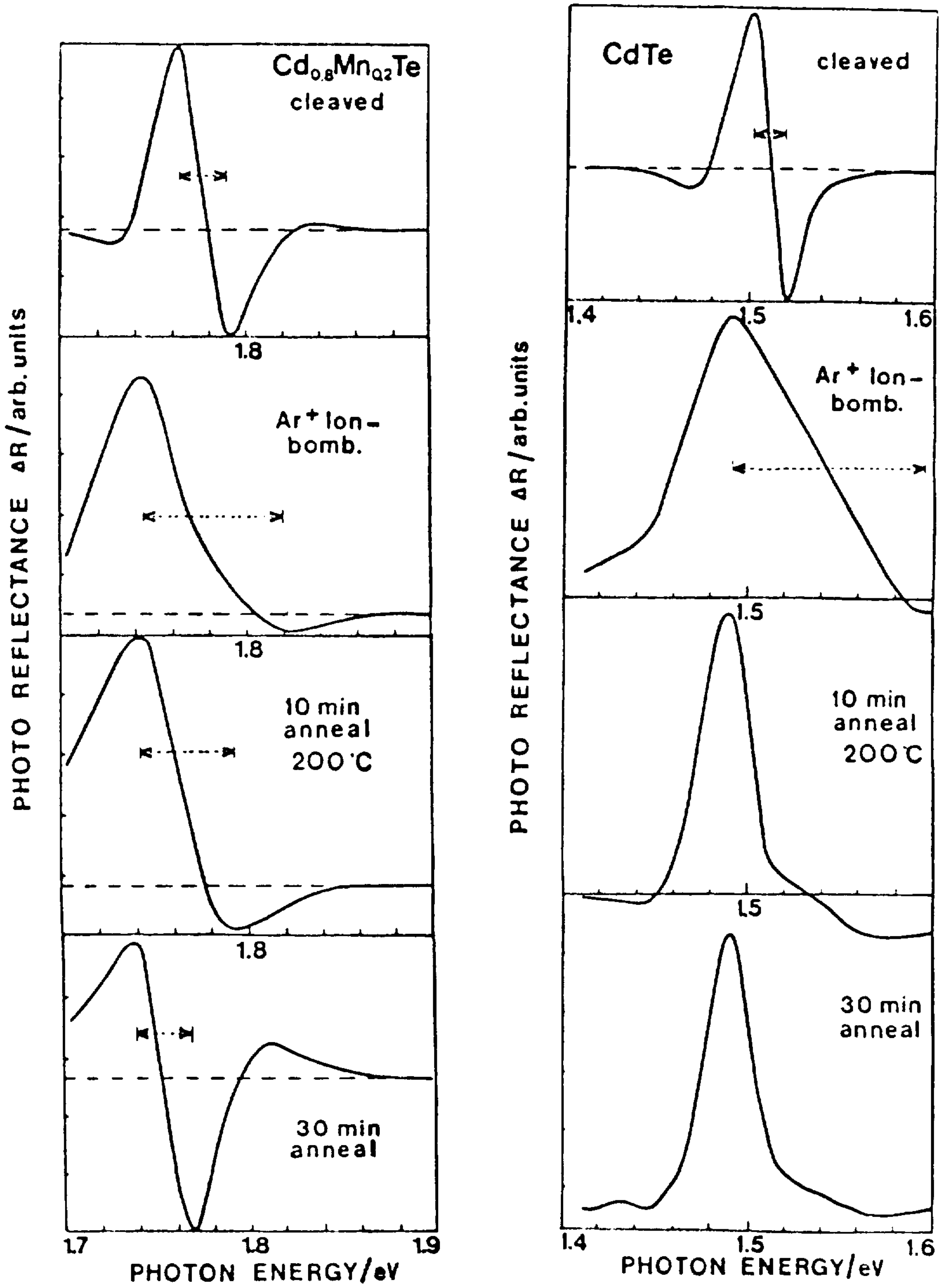

Figure 5. Line broadening and recovery of the photoreflectance signal after radiation damage and annealing of CdTe and $Cd_{1-x}Mn_xTe$[10]

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