Growth of Photovoltaic Semiconductors

E. YABLONOVITCH

Bell Communications Research, Navesink Research Center, Red Bank, NJ 07701-7040

G.B. STRINGFELLOW

Department of Materials Science, University of Utah, Salt Lake City, UT 84112

J.E. GREENE

Coordinated Science Laboratory, University of Illinois, Urbana, IL 61801

We assess the opportunities for improving the quality and lowering the cost of thin crystalline semiconductor films for photovoltaics. We find that novel growth and processing methods can lower the cost of crystalline semiconductor films to satisfy the economic conditions for a major expansion of the photovoltaic industry. The research requirements are in the areas of novel precursors for vapor phase growth, atomic layer epitaxy for unprecedented control, and the requirement for novel in situ and ex situ probes to ensure that the new growth methods are producing the utmost in photovoltaic material quality.

Key words: Atomic layer epitaxy, OMVPE, photovoltaics

INTRODUCTION

There is no law of physics which says that a thin crystalline film must be expensive. Indeed the question of production costs falls not within the domain of physics, but within the field of cost engineering. Generally, the cost of things is determined by size, weight, etc., and ultimately by those niggling practical details that real scientists prefer to overlook.

In the field of solar cells, we cannot avoid dealing with costs. Group III-V solar cells have always been respected for their high efficiency and performance, but they have generally been regarded as a high cost option. This assumption may now be changing. New thin film handling techniques, such as epitaxial lift off[1-4] (ELO), are making it possible to separate thin $Al_xGa_{1-x}As$ epitaxial films from their substrates. By reusing the substrates, we pay only for the epi-film itself, which can be as thin as 5000 Å in an optimized modern solar cell design. Such a thin layer is potentially very cheap. With very little mass per unit of area and per unit of performance, the material cost can be very low.

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Further, recent developments give more motivation for advanced III-V growth. Light-trapping allows a reduction in solar cell thickness from ~5 μm, increasing the practicality and cost effectiveness of the III-V option. Recycling of the growth feedstock, the reaction precursors, as is done in chemical plants, will reduce the costs down to the level of elemental costs only.

We present here some new research opportunities for applying modern growth concepts to photovoltaics. We must emphasize a need for a new cultural attitude among crystal growers if their work is going to lead to successful photovoltaic materials. They must now routinely test their materials for minority carrier lifetime and/or room temperature luminescence efficiency. To make this possible, new diagnostic tools, rapid, contactless, and nondestructive, will have to be developed. This is one of our major recommendations. To enforce this cultural attitude, proposals for new growth concepts should be accompanied by procedures for constant testing of the new materials and heterointerfaces for their photovoltaic Figures-of-Merit, namely, minority carrier lifetime, interfacial recombination velocity, and especially room-temperature luminescence efficiency.

NEW PRECURSORS FOR GROWTH OF III-V SEMICONDUCTORS

Probably the only viable epitaxial growth technique for mass production of the complex III-V and/or II-VI semiconductor structures, as required for future high-performance photovoltaic solar cells, is organometallic vapor phase epitaxy (OMVPE). However, a number of problems remain to be solved for OMVPE to reach its full potential. These present research opportunities will be discussed here.

The past few years have seen a remarkable convergence of the different vapor-phase growth techniques. Molecular beam epitaxy (MBE) became gas-source MBE (GSMBE), MOMBE, and chemical beam epitaxy (CBE). At the same time OMVPE has grown and strengthened. Today the unity of the different growth techniques is being recognized. Whether growth takes place in ultra-high vacuum or in ultra-high purity (Pd filtered) hydrogen gas is probably less important than the choice of precursor molecules. The only clear trend is moving away from elemental sources toward molecular reactant feedstocks for growth. This is providing exciting new technological opportunities for PV growth.

As an example of convergence, scientific information that is obtained in UHV by reactant gas dosing of a surface, can be applied toward growth in OMVPE using the same reactant gas. Scaling up the gas pressures toward OMVPE conditions will, in any case, be necessary for economical growth of photovoltaic materials. Therefore, while we will emphasize OMVPE, we do not mean to preclude UHV growth conditions, particularly for scientific studies.

Present Status of Precursor Technology

Organometallic vapor phase epitaxy has developed into the leading technique for the cost-effective production of III-V semiconductor structures for large-area devices, such as solar cells. It is now well-documented that OMVPE can be used to produce GaAs, InP, AlGaAs, GaInAsP, and related alloys with purity matching or exceeding that obtained by other competing techniques. It is also the most versatile technique, having been demonstrated for the production of essentially all III-V binary compounds and ternary and quaternary alloys containing aluminum, gallium, indium, arsenic, phosphorus, and antimony, including alloys with large miscibility gaps.[5] It has also been developed to provide atomically abrupt interfaces for the production of quantum wells, superlattices, and two dimensional electron gas structures with performance equal to the acknowledged early leader, molecular beam epitaxy.

Other practical improvements in the OMVPE technique for PV applications are also needed: (i) decreased carbon contamination, particularly in Al-containing materials, (ii) reductions in the hazard associated with particular precursors, particularly the Group V hydrides arsine and phosphine, (iii) dopants for n^+ and p^+ layers for the tunnel junctions required for tandem solar cells, (iv) novel techniques for highly controlled growth such as atomic layer epitaxy (ALE) and selective growth, and (v) the control of surface processes leading to interesting and potentially useful structures such as the (spontaneously ordered) "natural-superlattice" structures.

Substantial improvements in each of these areas is expected to be achieved by the use of improved precursor molecules. Until recently, choosing a precursor was largely an empirical exercise of trying the various chemicals selected from suppliers' catalogues to see which gave the best semiconductor layers. The precursors were generally of the type MR_n where M represents the Group III or V element of interest and R was largely limited to methyl or ethyl radicals or H radicals for the group V precursors. An early problem addressed by the development of new precursors was the extreme hazard associated with the use of the Group V hydrides, arsine and phosphine. This led to the development of the extremely successful new precursors tertiarybutylarsine (TBAs) and tertiarybutylphosphine (TBP).

Only during the last few years have the serious limitations imposed on OMVPE by the restricted choice of source molecules begun to be realized. Conversely, we are beginning to realize the tremendous opportunities afforded by the development of novel precursors. In the future, design of the precursor molecules will become an essential part of the design of the overall epitaxial process. We are now entering the era of "designer" molecules where specific and distinct precursor molecules will be developed having the optimum characteristics for each of the various vapor growth processes using organometallic molecules: OMVPE, OMMBE, CBE, ALE, laser assisted OMVPE, and others.

The areas for future development of the OMVPE processes mentioned above are closely interrelated. The design of precursor molecules requires a detailed understanding of the surface reactions converting the precursor molecules into the desired III-V semiconductor, with a particular structure and including undesirable contaminants such as carbon. Thus, the understanding obtained from the studies of the nature of the III-V surface and the chemical and physical processes occurring during growth gives essential information for the intelligent design of new precursor molecules. This section gives a brief overview of the current status in these two areas as well as a brief assessment of some of the major research opportunities.

Current Status of Deposition Using Organometallic Precursors

Group III Precursors

The typical Group III precursors are the trimethyl compounds of aluminum, gallium, and indium. These materials are available in high purity form and have convenient vapor pressures; however, the relatively high reactivity of CH_3 radicals results in both high pyrolysis temperatures and carbon contamination of

the epitaxial layers, particularly for aluminum-containing materials and for CBE growth. Carbon contamination is successfully reduced using the triethyl group III alkyls.[6,7] However, the triethyl Group III alkyls are less convenient for OMVPE since they have much lower vapor pressures and are also much less stable. This leads to decomposition in the bottle during storage and to parasitic reactions that reduce the growth rate.

There is clearly a need for the development of novel Group III precursors for OMVPE that combine the best characteristics of the trimethyl and triethyl alkyls. A promising In precursor is ethyldimethylindium (EDMIn). TMIn is a solid, with a vaporization rate that is found to vary with time, while EDMIn is a liquid which yields high quality InP and GaInAs.[8,9]

A very recently developed liquid In precursor is triisopropylindium (TIPIn). It pyrolyses at relatively low temperatures, approximately 200°C lower than for TMIn.[10] Unfortunately, it has a vapor pressure of only 0.32 Torr at room temperature. It also appears to participate in prereactions that lower the growth efficiency. Nevertheless, it has been used, with arsine, for the growth of InAs layers with good surface morphologies at temperatures as low as 300°C. Preliminary indications are that the carbon contamination is an order of magnitude less than observed using either TMIn or EDMIn with arsine.[10]

New aluminum and gallium precursors are currently being developed that offer considerable promise for reduced carbon contamination in AlGaAs grown by OMVPE and CBE. Adduct compounds of the type[11] AlH_3-$N(CH_3)_3$ pyrolyze without the production of free methyl radicals and have been used to produce materials with low carbon concentrations. The vapor pressures of such adduct molecules are typically below the values desired for OMVPE, but should be acceptable for UHV techniques such as CBE. Naturally, the Group III hydrides would be excellent precursors, except for their instability. Formation of the adduct between alane and trimethylamine produces a marginally stable precursor. Unfortunately, it is a solid at room temperature. However, the similar AlH_3-$N(C_2H_5)_3$ is a liquid.[12] The related gallane compounds are even less stable than the alane compounds. Thus, they may be suitable only for CBE growth.[13]

An alternative approach is the use of novel trialkylgallium precursors such as triisoproprylgallium (TIPGa) and tritertiarybutylgallium (TTBGa).[14] These precursors have acceptable room temperature vapor pressures and are expected to give low carbon concentrations, due to the relative stabilities of isopropyl and teriarybutyl radicals. TIPGa has been successfully used for the CBE growth of GaAs and AlGaAs layers. However, TTBGa gives extremely slow growth rates, apparently because the bulky nature of the molecule prevents sticking on the GaAs surface.

Group V Precursors

AsH_3 and PH_3 are attractive precursors since they provide H radicals on the surface, leading to the removal of C-containing radicals from pyrolysis of the Group III precursors. The main disadvantage is the extreme hazard associated with their use. In the search for new Group V precursors, the requirement for high purity semiconductor layers imposes the constraint that the molecule contain at least one M-H bond, particularly when trimethyl-Group III alkyls are used. Empirically, two M-H bonds are better. However, as we examine specific precursor molecules, it will be seen that this rule is overly simple. On the other hand, increasing the number of M-H bonds increases the toxicity of the Group V precursors.[15]

TMAs, DMAs, TEAs, and DEAs are found to be unsuitable due to the resulting high levels of carbon contamination. This is partially due to the small number of H radicals per molecule (0 or 1) and partly due to the pyrolysis processes. Some processes, such as ß-hydrogen elimination, produce H radicals while eliminating the alkene molecules. Such processes are impossible for TMAs and DMAs, since they have no ß-hydrogens and are found not to be major pyrolysis pathways for TEAs and DEAs. For this family of molecules, by far the best purity levels are obtained using EAs[16] with two hydrogen atoms attached directly to the arsenic atom. The pyrolysis of ethylarsine produces highly reactive AsH_2 radicals on the surface, perhaps explaining the low carbon doping levels observed.

The organometallic Group V precursor giving the best results is TBAs. The results of detailed studies of carbon contamination levels indicate that TBAs gives even less carbon contamination than arsine.[17] This is consistent with the lower temperature pyrolysis of TBAs giving AsH and/or AsH_2 radicals.[18,19]

Several potentially useful OM arsenic precursors are currently being explored. The most promising is dimethylaminoarsine (DMAAs). This is one of the few arsenic precursors that can be used for the CBE growth of GaAs without precracking.[20] In fact, DMAAs is reported to act as a better carbon getter than arsine, allowing the growth of GaAs with low background doping concentrations using either TMGa or TEGa as the gallium precursor.

The most successful organometallic phosphorus OMVPE precursor to date is TBP. Recent studies have yielded InP grown using TMIn with high 77 K electron mobilities.[21] The pyrolysis of TBP has been studied extensively.[22] It occurs at much lower temperatures than for PH_3, mainly via homolysis, creating PH_2 radicals and relatively stable tertiarybutyl radicals. The PH_2 radicals reaching the surface react with methyl radicals from the Group III precursor, removing the carbon from the system. This is presumably responsible for the relatively low carbon concentration levels observed.

Very recently, several antimony precursors have been developed to replace the traditional precursors trimethylantimony (TMSb) and triethylantimony (TESb). A useful precursor is triisopropylantimony (TIPSb). It pyrolyzes,[23] by a combination of homolysis and ß-elimination reactions, at temperatures approxi-

mately 100°C lower than for TMSb. TIPSb has been used with TMIn and TMGa for the OMVPE growth of high quality layers of both InSb and GaSb.[24] Perhaps even more useful is tertiarybutyldimethylantimony (TBDMSb). The pyrolysis, at temperatures well below those required for TMSb, occurs by homolysis, producing t-butyl radicals and dimethylantimony. The data suggest that pyrolysis proceeds by disproportionation reactions,[25] without the production of methyl radicals. This is encouraging for avoiding carbon contamination of the epitaxial layers. High quality epitaxial InSb layers have been grown using TMIn and TBDMSb[26] at temperatures as low as 325°C, even lower than for TIPSb.

The design of precursors for OMVPE, GSMBE, OMMBE, and CBE is a promising area of research. TBAs and TBP are already gaining wide acceptance as replacements for arsine and phosphine in OMVPE, both because they are much less hazardous and also because they produce desirable growth characteristics such as more complete pyrolysis at lower temperatures. This gives the possibility of low temperature growth, using less of the valuable precursor, and giving better uniformity across a substrate with the inevitable temperature gradients. These precursors also give rise to lower carbon contamination levels. In all probability, specific precursors will be developed to ideally match the requirements for each type of growth system, i.e. OMVPE, CBE, ALE (atomic-layer epitaxy), photon assisted growth, etc. This work has begun and is expected to gain momentum. At an earlier stage of development is the control of surface processes by controlling the specific mobile species on the surface during growth. The precursor molecules would be selected to provide a specific, stable intermediate loosely bound to the surface, causing rapid surface diffusion to produce abrupt interfaces and ordered structures. More tightly bound species might produce less surface diffusion which would prevent or retard ordering. This second research area is thus closely coupled to research on surface processes. In fact, an understanding of the surface chemistry is absolutely essential to the intelligent design of precursors for specific applications.

Future Research Opportunities—Novel Precursors

A promising research area is the development of precursors for ALE. Presently, the temperatures when saturation occurs, (i.e. one monolayer is grown in each cycle independent of time, temperature, and input reactant pressures) is too low.[27] This results in GaAs with poor minority carrier properties. In addition, the carbon contamination levels are too high.[28] New precursors are required having higher stability than TEGa and TMGa, permitting higher temperature ALE, and presumably better minority carrier lifetime, a specific PV requirement. The radicals produced during pyrolysis must either not contain carbon or be stable enough to leave the surface without producing carbon in the epitaxial layer.

Another area requiring more stable precursors is the scaling-up of reactors for large-scale PV production. In the semiconductor industry, this is frequently accomplished by pushing the thin film deposition process into the kinetically limited growth regime where mass transport need not be carefully controlled. Stacked wafers have the same growth rate as long as the temperature is uniform. Furthermore, reactor throughput scales with reactor volume rather than area. Moving into the kinetically limited growth regime requires more stable Group-III precursor molecules, an area not currently being addressed in the research community but essential for PV. Volume growth scaling of reactors would have a revolutionary impact on the prospects for economical PV.

Selective-area growth will be useful for advanced, high performance PV devices to allow selective doping of only the areas directly beneath the point contacts. This may be accomplished by the use of dopant precursor molecules that pyrolyze only in the presence of an external energy source, such as a photon beam. These precursors must be designed to be stable at the growth temperature and to have a high absorption cross section at the laser wavelength used.

A research direction aimed at solving immediate industrial needs is the development of improved precursors for heavy n- and p-type doping. Carbon has been successfully used in CBE as a nonmobile acceptor in GaAs and AlGaAs at levels exceeding 10^{20} cm^{-3}. Less success has been achieved in OMVPE, mainly because the atomic hydrogen released on the surface by the Group V precursors (AsH_3, TBAs, etc.) combines with the organic radicals to produce volatile alkanes. Thus, a precursor specifically designed to give carbon in the epitaxial layer is required. Similarly, improved precursors for heavy n-type doping without adverse side effects is required. An additional short-term objective is the continuation of present work to produce even less hazardous As precursors than TBAs.

ATOMIC LAYER EPITAXY

Atomic-layer epitaxy (ALE) is a cyclic vapor-phase growth technique which incorporates self-limiting kinetic processes resulting in the deposition of θ monolayers (for an elemental material), or θ bilayers (for a compound), per growth cycle in which $\theta \leq 1$.[29] In the case of III-V and II-VI compound semiconductors, ALE has been accomplished by the sequential introduction of gas-phase molecular precursors whose heterogeneous reactivities depend upon the surface termination.[29,30] An example that has received significant attention in the past few years is GaAs(001) ALE using trimethylgallium [TMGa, $Ga(CH_3)_3$] and arsine (AsH_3) as reactants in an OMVPE reactor.[29] The growth sequence involves adsorbing 1 monolayer (ML) of TMGa on an arsenic-stabilized GaAs(001)4 × 2 surface under deposition conditions such that TMGa adsorbs only on As sites and does not form a multilayer. Thus, while a minimum exposure is required to form the monolayer, additional TMGa exposure has

(ideally) no effect. The TMGa flow is then halted and the gallium-containing surface layer exposed to AsH_3 which reacts to form a bilayer of GaAs while unwanted CH_x reaction products desorb. The deposition conditions are chosen such that the sticking probability of excess AsH_3 on an As-terminated surface is essentially zero. Although the reaction path is not understood in detail, chemisorption of TMGa must involve the scission of at least one Ga-C bond as one or more CH_3 radicals are desorbed, or adsorbed at adjacent sites and then desorbed through further reactions with TMGa. AsH_3, which is a much more powerful reducing agent in this case than H_2,[31] plays an important role in this process by supplying atomic hydrogen to react with adsorbed TMGa and liberate hydrocarbon radicals.

There are several potential advantages of ALE for device applications. The technique offers wide process parameter windows. As noted above, precursor gas exposures can be varied over extended ranges with little or no effect on film growth kinetics. The process steps are exothermic and growth is inherently in the surface reaction limited (rather than mass-transport limited) regime. Since the deposition rate is kinetically self-limiting, the film thickness, which is only dependent upon the number of gas exposure cycles, can be controlled to a high degree of accuracy. In addition, the process lends itself to obtaining a high degree of film thickness uniformity not only over large horizontal surfaces but, because of rate-limited kinetics, along vertical side walls as well. The cyclic nature of the deposition process provides the potential for the growth of materials with extremely narrow (approaching 1 ML) single or alternating doping spikes (so-called δ-doping).[32] Selective deposition is possible on masked substrates.

For photovoltaics, ALE offers the possibility of synthesizing new metastable phases in thin layers. These could be used in hetero-contacts, surface passivating window structures, tunnel contacts between layers of tandem cells, etc. However, ALE would probably be too slow for the economical growth of thick absorber layers.

There are presently a number of serious problems preventing implementation of III-V ALE in PV, including the fact that the surface reaction path is not well understood for GaAs and not understood at all for other III-V compounds and alloys. Although UHV experiments involving standard surface science probes such as modulated-beam mass spectrometry (MBMS), temperature-programmed desorption (TPD), high-resolution electron-energy loss (HREELS), and x-ray photoelectron spectroscopy (XPS) have been carried out using pulsed beams and known exposures of standard precursors such as TMGa on well defined surfaces, much more needs to be done. For example, multiple-internal reflection infra-red spectroscopy (MIRS) is a particularly powerful probe with very high chemical specificity that has not been widely applied to these problems. Proximity probes such as scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS), when used in combination with surface-science techniques providing area-averaged chemical information can be very powerful in yielding local topographical and chemical information. Results from the above experiments should be extended to encompass radical beams [e.g. $Ga(CH_3)_2$ and $Ga(CH_3)$, in addition to TMGa] in order to more closely couple with in-situ probe results obtained during ALE growth in atmospheric OMVPE reactions. The latter measurements should be carried out using the nonhigh-vacuum probes discussed in the section on Probing Growth.

The understanding gained from the combination of the above surface science and in-situ experiments during deposition will eventually lead to a detailed model of the reaction path which in turn can be used to better define the search for tailored precursors for use in III-V ALE. Parallel experiments on AlAs, for which no ALE reaction route exists, are required to develop new precursors for this compound. This overall approach can then be extended to other III-V PV candidates such as the phosphides. More stable ALE precursors are also needed to overcome other problems present with III-V ALE: high carbon contents in deposited layers, narrow growth temperature plateaus, and low maximum growth temperatures before kinetic-limitations are lost.

Recently, surface-science investigations[33,34] of the interaction of Si_2H_6 with clean Si(001)2 × 1 and Ge(001)2 × 1 surfaces has led to the development of a UV-photostimulated silicon ALE process.[35] The silicon ALE deposition rate R per growth cycle remains constant at 0.43 ML (1 ML = 6.8×10^{14} cm^{-2}), over a wide range of deposition parameters: growth temperature (T_s = 180 – 400°C), Si_2H_6 exposure peak pressure during gas pulse (71.5 mTorr), KrF UV laser density (E = 250 – 450 mJ cm^{-2}), and number of UV laser pulses per cycle. A film growth model, based upon the results of adsorption/surface-dissociation/desorption experiments using electron energy-loss spectroscopy (EELS), reflection high energy electron diffraction (RHEED), STM, and STS, together with Monte Carlo simulations has been developed. Si_2H_6 is dissociatively adsorbed on Si dangling bonds as two silyl (SiH_3) radicals that subsequently dissociate across dimer rows to silylene (SiH_2) and hydrogen. The ALE deposition rate R is limited to 0.43 due to site blocking and stearic hindrance during the adsorption and dissociation steps. The hydrogen passivated surface is then reactivated photothermally during the laser pulse.

Understanding of Si-H and Ge-H surface chemistry gained in the above types of experiments provides directions for future research in the development of new high bandgap layers such as $Si_{1-x}C_x$ and $Si_{1-x}N_x$ alloys, grown epitaxially by ALE on silicon. There is a need, particularly in high efficiency (28%) C-Si concentrator cells for a replacement for the passivating thermal SiO_2 layer, whose surface recombination velocities degrades with time and ultraviolet exposure. The potential advantages of ALE in the growth

of these alloys are related to the fact that high surface adatom mobilities can be achieved at relatively low steady-state growth temperatures minimizing lattice atom mobilities.

PROBING GROWTH

In-Situ Probes

Development of a detailed understanding of the growth processes involved in the production of epitaxial layers using organometallic precursors is absolutely essential for the follow reasons:

(i) The development of strategies and techniques for moving organometallic deposition techniques into the more aggressive regime of the high growth rates and high throughputs required for cost-effective PV production can only be accomplished through a much more complete understanding of the physics and chemistry of the growth process.

(ii) The rational design of precursor molecules requires a detailed understanding of heterogeneous reaction processes and kinetics.

(iii) The development of special techniques such as ALE and photon assisted growth by trail and error techniques, without a fundamental understanding of the basic surface reactions is inefficient and, in fact, likely to lead in the wrong research direction.

(iv) The microscopic nature of the semiconductor produced is extremely dependent on the nature of the surface processes. For example, insufficient surface mobility leads to defected layers with poor minority carrier properties. Surface reconstruction and step propagation during growth are believed to result in atomic-scale ordering in epitaxial layer of alloy semiconductors.[36] Such ordering may have profound effects on the electrical and optical properties of the resulting layers.

In-situ probes, such as reflectron high energy electron diffraction (RHEED), have assisted significantly in the development of an understanding of the physics and chemistry of MBE growth, such as surface reconstruction and the layer-by-layer growth rate.[37] Not only is such information valuable for monitoring the epitaxial growth, but perhaps more importantly, it has led to marked advances in our understanding of the surface processes occurring during epitaxial growth that may be applicable to all growth techniques. Unfortunately, in-situ probes for monitoring the OMVPE growth process have been lacking. It is vital that in-situ techniques be developed for the characterization and monitoring of the OMVPE growth process. Electron diffraction techniques are precluded by attenuation of electron beams in the OMVPE ambient. However, optical techniques have recently become available that appear to give similar information.[38] In addition, synchrotron x-ray scattering from the surface can be used to give information similar to that obtained from RHEED measurements.[39]

For chemists, infrared spectroscopy has always been a powerful structural probe. Multiple internal reflection infrared spectroscopy is sensitive surface probe. It can operate in-situ, but not necessarily at the full growth temperature due to free carrier absorption in the semiconductor substrates. Reflection difference spectroscopy (RDS) is found to be sensitive to the detailed nature of the semiconductor surface.[3] Thus, distinct spectra are obtained for each of the common surface reconstructions observed using RHEED spectroscopy. The same spectral features are observed for surfaces held under various conditions at atmospheric pressure. Thus, the reconstructions existing during OMVPE growth have recently been identified.[40] This is extremely significant, since surface reconstruction is believed to drive the surface processes leading to ordering in III-V alloys.[41]

However, the nature of the surface during OMVPE growth is still a topic of heated debate, since in-situ x-ray scattering measurements performed using synchrotron radiation indicate the lack of surface reconstruction during growth.[4] This topic is of central importance for the understanding of the OMVPE process and is still in infancy. RDS and the related surface photo-absorption (SPA) are currently being used to study the pyrolysis of various Group III and Group V precursors on III/V surfaces.[42] These represent the first direct studies of surface pyrolysis reactions outside of a UHV chamber.

A most important area of future work is the discovery of the fundamental processes occurring at the surface during OMVPE. This will involve both surface studies of chemical reactions, including the determination of rate constants, as well as studies of the physical processes occurring at the surfaces such as surface reconstruction, the nature and motion of steps and kinks, the nucleation of two dimensional islands, the diffusion of surface species and the control of diffusion coefficients by controlling the nature of the surface species. These extremely difficult and complex tasks will require many man years of effort. However, without this understanding, we can never hope to understand and control the OMVPE process.

Ex Situ Probes

It is worth emphasizing the need to develop effective ex situ minority carrier lifetime probes. This is needed at every reactor and growth facility in order to tell the grower whether he is doing well, and making good material. The emphasis has to be on rapid (15 minutes or less) feedback to the crystal grower of the nonradiative lifetime component. Then he can feed the information directly into his next growth run. Existing rapid diagnostic probes in the electronics industry tend to focus on other properties, such as majority carrier properties, which are not as relevant to photovoltaics. It is very important that these new probes be contactless in order to avoid contamination of the freshly produced material. In addition, it is essential that the probe should be nondestructive so that it can become a standard on-line process evaluation tool. Another important point is the need for wide distribution and availability of these diagnostic instruments. It should not be necessary to hire a

Ph.D. or any full time staff member to operate such a system. Further the equipment cost should not be a deterrent to the universal adoption of these non-destructive testing tools.

It is particularly challenging to measure the relevant nonradiative lifetime in the presence of dominant radiative recombination. While this is an indication of outstanding material quality, for which the crystal grower should be congratulated, that is no time for complacency. Even better material quality must be pursued, making the non-radiative component an ever smaller fraction of the radiative recombination rate. New diagnostic techniques will have to be developed to permit such testing.

Most existing diagnostic tools are not entirely satisfactory. Surface photovoltage is too slow and does not lend itself to modern thin double heterostructures. Laser pumped photoconductivity, monitored by microwaves or by a radio-frequency coil, is better, but it has poor spatial resolution, and cannot separate radiative and nonradiative components. What is needed is a new tool, similar in simplicity to the "POLARON," an electrochemical etching and depletion capacitance probe which exists in almost every growth facility for depth profiling. Since solar cells are opto-electronic devices, a new type of all optical probe, probably with time resolution, is called for. The essential point is that it should appeal to growers and be universally adopted.

SUMMARY

There are significant opportunities for the growth of crystalline semiconductor thin films of higher photovoltaic quality and lower cost. These research opportunities are in novel precursor molecules for vapor phase growth, atomic layer epitaxy for unprecedented growth control, and requirements for novel in situ and ex situ diagnostics to ensure that the novel growth conditions are producing good quality materials at economic growth rates.

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