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[57] ABSTRACT

A method for preparation of a dilute magnetic semiconductor (DMS) film is provided, wherein a Group II metal source, a Group VI metal source and a transition metal magnetic ion source are pyrolyzed in the reactor of a metalorganic chemical vapor deposition (MOCVD) system by contact with a heated substrate. As an example, the preparation of films of Cd1-xMnTe, wherein 0.3 ≤ x ≤ 0.7, on suitable substrates (e.g., GaAs) is described. As a source of manganese, tricarbonyl (methylcyclopentadienyl) manganese (TCPMn) is employed. To prevent TCPMn condensation during the introduction thereof into the reactor, the gas lines, valves and reactor tubes are heated. A thin-film solar cell of n-i-p structure, wherein the i-type layer comprises a DMS, is also described; the i-type layer is suitably prepared by MOCVD.

30 Claims, 7 Drawing Sheets
OTHER PUBLICATIONS


FIG. 1
PREPARATION OF DILUTE MAGNETIC SEMICONDUCTOR FILMS BY METALORGANIC CHEMICAL VAPOR DEPOSITION

BACKGROUND OF THE INVENTION

1. Origin of the Invention

The invention described herein was made in the performance of work under a NASA contract, and is subject to the provisions of Public Law 96-517 (35 U.S.C. 202) in which the Contractor has elected not to retain title.

2. Field of the Invention

This invention relates to dilute magnetic semiconductors, and more particularly, to preparation of a semiconductor film of the CdTe-MnTe alloy system by metalorganic chemical vapor deposition.

3. Description of the Relevant Art

Dilute magnetic semiconductors (DMS) are pseudobinary Group II-Group VI semiconductors in which a fraction x of the Group II elemental sites are occupied by a transition metal magnetic ion, usually Mn. The CdTe-MnTe alloy system is perhaps the most extensively studied member of this class of materials. Single phase solid solutions of this II-VI semiconductor with zincblende structure are formed in the system Cd$_{1-x}$Mn$_x$Te, wherein 0≤x≤0.7. The energy gap at room temperature (E$_g$=1.50+1.34×eV) and lattice constant (a$_0$=6.487-0.149×Å) vary linearly throughout this range, even though MnTe has a different structure (nickel arsenide) from that of CdTe (zincblende). The presence of the paramagnetic manganese ions in the host lattice (CdTe) gives rise to interesting magnetic and magneto-optical properties because of spin-exchange interactions with conduction band electrons and valence band holes which modify the band structure. Such interesting phenomena include a giant Faraday rotation near the fundamental absorption edge, an extremely large negative magneto-resistance, Stokes-shifted spinflip Raman scattering, and very large electronic g-factors.

Heteroepitaxial thin films of (CdMn)Te have heretofore been deposited by molecular beam epitaxy (MBE), primarily on GaAs substrates. Subsequently, multiple quantum well and superlattice structures also have been prepared. These structures have exhibited strong photoluminescence, stimulated emission and magnetically tuneable lasing action. It is well known, however, that MBE deposition is not the method of choice for commercial-scale preparation of components for photovoltaic and x-ray detection systems, and x-ray waveguide devices.

Ionized cluster beam deposition methods require the use of high vacuums, although not as high as with MBE methods. Moreover, deposition rates are generally low, and there are problems with deposition area and uniformity.

There has been to date no report of (CdMn)Te deposition by MOCVD techniques, although high-quality heteroepitaxial CdTe films have been grown on GaAs, InSb and sapphire substrates. One practical reason for this has probably been the lack of a reasonably high vapor pressure metal alkyl source for Mn.

STATEMENT OF INVENTION

It is an object of the invention to provide a method for preparation of (CdMn)Te and other ternary dilute magnetic semiconductors which would permit treatment of larger area substrates and growth of the required thicknesses in less time.

It is another object of the invention to provide a method whereby (CdMn)Te and other ternary DMS can be prepared without the need for expensive high-vacuum capital equipment, such as is required for MBE deposition.

It is another object of the invention to provide a method for heteroepitaxial growth of semiconductor layers of alloy systems, such as (CdMn)Te, which will permit commercial-scale preparation of DMS films in an efficient and reproducible manner.

In accordance with these and other objects, the invention comprises in a first aspect thereof a method for preparation of a semiconductor layer by heteroepitaxial growth of a dilute magnetic semiconductor alloy on a suitable substrate by metalorganic chemical vapor deposition. The substrate in the deposition zone of a metalorganic chemical vapor deposition system is heated to an elevated temperature. A gas mixture comprising a carrier gas and sources of Group II metal (e.g., Cd, Zn and Hg), Group VI metal (e.g., Te, S and Se) and transition metal magnetic ion (e.g., Mn and Fe) are introduced into the reactor. By contacting the gas mixture with the heated substrate, the metal sources are pyrolyzed and a ternary alloy DMS film is formed.

In a preferred embodiment of the inventive method, the DMS is an alloy of the system Cd$_{1-x}$Mn$_x$Te, wherein 0≤x≤0.7. Dimethyl cadmium (DMCd), diethyltellurium (DET) and tricarbonyl (methylcyclopentadienyl) manganese (TCPMn) are suitable metalorganic source materials. To accommodate the use of TCPMn as a manganese source, heated gas lines, valves and reactor tubes are employed. In addition, the TCPMn is heated to provide the required vapor pressure.

In accordance with another aspect of the invention, a thin film solar cell of an n-i-p structure is provided, wherein the i-type layer comprises a dilute magnetic semiconductor. The i-type layer is suitably prepared by an MOCVD method. The preparation of such a solar cell with a Cd$_{1-x}$Mn$_x$Te insulator layer (x=0.15) and its practical applications in a tandem cell system are disclosed.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 illustrates the optical transmission curve for a CdTe film and two Cd$_{1-x}$Mn$_x$Te films wherein x=0.2 and x=0.3, respectively.
FIG. 2 illustrates the x-ray diffraction curve for a 2-μm thick Cd₃Mn₂Te film grown on a (100) GaAs substrate.

FIG. 3 is the photoluminescence intensity curve of a Cd₃Mn₂Te film grown on a (100) GaAs substrate when excited at 10K by a 488 nm wavelength argon laser.

FIG. 4 is a photograph of a Cd₃Mn₂Te layer on GaAs illustrating its specular characteristics.

FIG. 5 is a scanning electron microscope (SEM) micrograph of a Cd₃Mn₂Te layer on a (100) GaAs substrate misoriented 2° toward the (110) direction, showing surface morphology at a tilt angle of 70° C.

FIG. 6 illustrates a tandem solar cell including a Cd₁₋ₓMnₓTe layer prepared in accordance with the invention.

FIG. 7 illustrates a suggested energy band line-up at zero bias for a Cd₁₋ₓMnₓTe layer wherein x=0.15, based on experimental valence band offsets obtained by synchrotron radiation photoemission.

DETAILED DESCRIPTION OF THE INVENTION

This invention demonstrates for the first time the feasibility of heteroepitaxial growth of DMS films, such as Cd₁₋ₓMnₓTe films, on suitable substrates, such as (100) GaAs substrates, by atmospheric or reduced pressure MOCVD. These products exhibit crystallographic properties similar to those of MBE-grown films. Films with Mn atomic fractions up to 55% have been grown with uniform Mn concentration throughout the film, by suitable adjustment of operating parameters such as gas flow rates in a manner well-known in the MOCVD field. In addition, the inventive method permits the deposition of other DMS films in an efficient and economical manner.

On account of their desirable properties, DMS films prepared by the method of the invention have a wide range of practical applications, as is well known in the art. As an example, deposition of (CdMn)Te films with a bandgap energy of about 1.7 eV (x=0.15) on CdS thin films for use as a higher bandgap solar cell on a cascaded multiple-junction tandem solar cell is illustrated. Through the use of suitable masks, moreover, it is possible to coat only portions of the substrate, thereby facilitating manufacture of patterned products.

The MOCVD deposition may be carried out at atmospheric or reduced pressure. In fact, the use of lower pressures (on the order of about 0.1 atmospheres) may in certain instances provide products with superior morphology and uniformity in thickness over large areas. The use of such reduced pressures has received increasing attention of late in the MOCVD of Group III-V materials. While it is a particular advantage of the inventive method that DMS films may be grown at atmospheric pressure, the use of moderately reduced pressures does not present technical difficulties which would inhibit the development of commercial-scale methods, at least not to the extent as is the case with the significantly more stringent vacuum requirements of MBE or ionized cluster beam methods.

As is well known in the art, a wide range of substrates may be employed in addition to the GaAs substrate described in the examples. On account of the good lattice match, InSb is particularly suitable. In addition, sapphire and especially silicon substrates are of high technological interest. Moreover, buffer layers (for example, CdTe) or superlattices (e.g., CdTe/ZnTe, (CdMn)Te/CdTe and (CdZn)Te/CdTe) of appropriate thicknesses may suitably be employed to improve surface properties and crystallinity.

A further parameter which permits the preparation of products having a range of different properties is the choice of specific orientation relationship. In addition to a (100)/GaAs substrate relationship, for example, off-axis orientation of the exemplary (100) GaAs substrate may suitably be introduced in the (110) or (111) directions. At present, off-axis orientations of up to 13° or more toward the (110) or (111) direction are contemplated with GaAs substrates. Si substrates having both (100) and (111) orientations may also be employed.

The nucleation and growth stages of the DMS layers are affected by a variety of factors, including initial gas flow conditions and substrate surface characteristics and temperature. As in conventional MOCVD procedures, flow rates and linear flow velocities may be varied within fairly broad ranges, both for individual sources and for transport gas, so as to change the composition of the final product and/or modify the growth rate. Linear flow velocities on the order of about 1-10 cm/sec for combined metal source(s)/transport gas would be suitable, for example, in a typical growth system as is described in the examples. As the morphology of the substrate surface can have a significant effect on the orientation relationship, preparation of products having optimum characteristics may in some instances require surface treatment of a given substrate, such as pre-cleaning or in-situ oxide removal. In particular systems, additional factors specific to such systems will also influence growth orientation and product morphology. For example, Te passivation of Ga and As bonds may, in some situations, suggest preintroduction of the Te gaseous source in MOCVD of (CdMn)Te on GaAs.

In principle, growth orientation and surface morphology in the preparation of these DMS systems have a direct influence on the electronic properties of the final product, as a consequence of the resultant interfacial atomic arrangements and generation of faults in the system (e.g., misfit dislocations, stacking faults, microtwins, etc.). By suitable selection in any given instance, it is possible to reduce the density of interfacial dislocations. Control of the dislocation density is important in many systems, for example, to reduce interdiffusion of elements from different layers in a multi-layer system via pipe diffusion mechanisms. By controlling the growth of a layer so that it has a particular orientation, it is possible in many instances to obtain a product having a greatly reduced number of defects. Depositions under reduced pressures in particular may permit preparation of ultra-thin layers having abrupt interfaces. In addition, in multiple layer or superlattice structures, the thickness of intermediate layers may also influence sample growth; as an example, a CdTe intermediate layer of a thickness of 200 Å or less will induce pseudomorphic (and thus, substantially dislocation-free) growth. If properly grown (i.e., with appropriate layer thicknesses and very abrupt interfaces), such structures may serve as effective dislocation filters.

As in conventional MOCVD of binary films, a wide range of metal sources and carrier gases may be employed. For example, suitable Cd sources include diethyl- and diethyl cadmium; Te sources include diethyl- and dibutyltellurium; and carrier gases include hydrogen, nitrogen, argon and helium. In addition to other metalorganic source materials, moreover, certain inorganic sources (e.g., metal carbonyls) may be
suitable in some instances. According to the inventive method, it is possible to introduce a variety of dopants, such as As, P and Sb (for p-type layers) or Ga, In and Cl (for n-type layers). By adjustment of, e.g., source temperature and flow rates, a variety of desired elements may be introduced into the particular system of interest in a manner well within the skill of a person familiar with MOCVD methods employing the corresponding source materials.

The invention may be better understood with reference to the accompanying examples, which are provided solely for purposes of illustration and should be viewed as in no way limiting the scope of applicants' invention.

EXAMPLE 1

To illustrate the method of the present invention, the following exemplary description is provided of heteroepitaxial growth of Cd$_{1-x}$Mn$_x$Te films on (100) GaAs substrates by atmospheric pressure MOVCVD.

The growth system used comprised a horizontal quartz reactor tube operating at atmospheric pressure with an RF-heated graphite susceptor. The metallicorganic sources for the Cd and Te were dimethylcadmium (DMCd) and diethyltellurium (DET$_e$), respectively. The transport gas was palladium-diffused high purity $\text{H}_2$. The DMCd source was held at a temperature of $0^\circ$C. and the DET$_e$ source at $27^\circ$C. The total flow rate of H$_2$ and metalorganics was about 4 l/min, corresponding to a linear flow velocity of about 3 cm/sec over the substrate.

Films of CdTe were first grown at temperatures of 400-450$^\circ$C on GaAs substrates (100) misoriented 21' toward the (110) direction. The substrates were cleaned in organic solvents and etched with a H$_2$SO$_4$-H$_2$O$_2$-H$_2$O solution (5:1:1) for 30 seconds. After loading the substrates, the system was pumped down to about 50 micro-Torr and then brought up to atmospheric pressure under H$_2$, at which time the substrate was heated to the growth temperature. The partial pressures of the Cd and Te sources during deposition were typically about 8 x 10$^{-3}$ atm and 1.6 x 10$^{-4}$ atm, respectively. Films of CdTe with thicknesses of 2 mm were deposited with excellent surface morphology and crystallinity. Also, the films showed no indication of or peeling. The films were deposited on (100) GaAs substrates excited by a 488 nm argon laser. FIG. 3 shows the spectrum observed for a Cd$_{1-x}$Mn$_x$Te film at T = 10K. The full width at half maximum (FWHM) of about 33 meV is an indication of the good crystalline quality of the layer.

The surface topography of CdTe films on GaAs was featureless when viewed with a light microscope and showed no indication of cracking or peeling. The films also presented a "mirrorlike" reflectance to the naked eye with no hazy areas. However, when Mn was added to the films, haziness was observed in some cases. Attempts to modify the morphology with changes in the carrier gas flow rate, the mole fraction ratio of Te to Cd/Mn, and substrate temperature have not yet provided a conclusive relationship among these factors; nevertheless, (CdMn)Te films having a smooth and mirrorlike surface morphology have been obtained, such as illustrated in FIG. 4. This suggests that the milky appearance of some films is probably related to aspects of the process and system during preliminary experiments, rather than being an inherent material problem. For example, the importance of remaining below 440$^\circ$C when growing CdTe on GaAs MOVCVD has been reported in the literature, due to suspected formation of Te crystallites on the substrate and the introduction of Te above that temperature. Nonetheless, for all practical purposes films of a suitable quality are routinely prepared by the inventive method. A closer look at the surface of an exemplary (CdMn)Te film by a scanning electron microscope (FIG. 5) shows a very light ripple effect with features having dimensions of only about several thousand angstroms.
This describes the preparation of high efficiency thin-film solar cells. Conventional solar cells having a single bandgap $E_g$ are limited in conversion efficiency since absorbed photons with energy in excess of $E_g$ have that excess energy wasted as heat. However, even after considering additional practical losses, such as series resistance, contact shadowing and processing-induced defects, efficiencies as high as 23 percent at one sun intensity have been obtained for single crystal laboratory cells made from Si or GaAs. Thin-film solar cells, highly desirable because of their potential low cost, have considerably lower efficiencies. This is due mainly to material imperfections, which lead to recombination losses and to non-ideal $p/n$ junction characteristics. The highest reported laboratory efficiencies are in the 11-12 percent range for both CdTe/CdS and CuInSe$_2$/CdS heterojunction thin-film solar cells.

One method proposed for further increasing efficiencies is that of optically stacking in tandem two or more junction devices having different values of $E_g$ (J.C.C. Fan et al., Proc. 16th Photovoltaic Specialist Conf., p. 60, 1982). The uppermost (sunlit side) thin film material must absorb higher energy photons while transmitting most of the longer wavelength photons for absorption in the lower cell. The stacked cells can be either two-terminal monolithic devices (presenting particularly difficult materials growth and processing considerations), or four-terminal devices, formed by joining single-junction devices, deposited on conductive oxide-coated glass substrates in optical contact.

The optimum p-type doping should be about 10$^{15}$ cm$^{-3}$, which is the same in Example 1. Films of CdTe were first deposited on SnO$_2$-coated glass substrates purchased from the MOCVD reactor and a heat treatment in air for CdTe deposition showed a reasonably sharp interface between the CdS and CdTe. The sputter etching rate during this profiling was about 175-200 A/minute. More importantly, good performance, and hence, poor open circuit voltage ($V_{oc}$) and conduction voltage-capacitance-voltage characteristics were measured in the usual way.

After optimization of CdTe (and subsequently, (CdMn)Te) deposition parameters on glass and crystalline GaAs substrates, depositions were made on poly-crystalline CdS films. Because of concerns that interdiffusion at the interface might cause leaky heterojunction performance, and hence, poor open circuit voltage ($V_{oc}$), substrate temperatures were initially kept as low as possible (i.e., about 410°C). The thickness of CdTe was typically about 1.5-2.0 $\mu$m after 30 minutes of growth at that temperature. A depth profile of the solar cell structure after annealing and ZnTe overcoating showed a reasonably sharp interface between the CdS and CdTe. The sputter etching rate during this profiling was about 175-200 A/minute. More importantly, good junction performance was observed with a value for $N_{c0}$ of 675 mV and a short-circuit current density ($J_{sc}$) of 50-55 percent prevented an efficiency of 10 percent or greater. The low fill factor, apparently due to high series resistance, would be preferred, though not necessary, since the growth rate of the (CdMn)Te would be higher.

After optimization of the operating parameters, several solar cell structures were fabricated having efficiencies over 9%. One set of samples from one 4 cm$^2$ substrate averaged 9.4% efficiency, showing good dark I-V characteristics. The values of $V_{oc}$ (657 mV) and $J_{sc}$ (22.1 mA/cm$^2$) compare very favorably with the best reported values for CdTe/CdS cells using alternative CdTe deposition techniques. Only a low fill factor of 50-55 percent prevented an efficiency of 10 percent or greater. The low fill factor, apparently due to high series resistance, could be caused either by the fact that the CdTe layer thickness (2.0-2.1 microns) for that sample is larger than the depletion width and/or by degradation of the SnO$_2$ conductive coating during the MOCVD growth. Reflecting the increased magnitude of $J_{sc}$, spectral response measurements of the sample
showed average quantum efficiency of 85% between 500 and 800 μm.

The preliminary photovoltaic results of similar structures consisting of Cd1.5Mn0.5Te for CdTe confirmed the feasibility of such a system. Consideration of band effects make the CdS/CdTe or (CdMn)Te/ZnTe n-i-p solar cell structure very attractive because of the low offsets, and thus, low potential barriers for minority carriers, along with large offsets for majority carriers which may act as "mirrors", reducing interface losses. The most useful aspect of the n-i-p structure, when properly implemented, is that the p-type doping and ohmic contacting problems encountered with CdTe-related compounds may be avoided.

What we claim is:

1. A method of preparing a dilute magnetic semiconductor film on a substrate in a deposition zone of a reactor of a metalorganic chemical vapor deposition system, said method comprising:
   - heating the substrate in the deposition zone to an elevated temperature in the range of about 410° to about 450° C;
   - introducing into the reactor a gas mixture comprising a Group II metal source, a Group VI metal source a transition metal magnetic ion source, and a carrier gas;
   - forming said film by contacting the substrate with said gas mixture, thereby pyrolyzing the metal sources and forming a ternary alloy, whereby the magnetic ion source is incorporated into the lattice structure of said film.

2. A method according to claim 1, wherein said Group II metal is selected from the group consisting of Cd, Zn and Hg.

3. A method according to claim 1, wherein said Group VI metal is selected from the group consisting of Te, S and Se.

4. A method according to claim 1, wherein said transition metal magnetic ion is selected from the group consisting of Mn and Fe.

5. A method according to claim 1, wherein said dilute magnetic semiconductor is Cd1-xMnxTe, in which 0<x≤0.7.

6. A method according to claim 5, wherein said Group II metal source is selected from the group consisting of dimethyl- and diethylcadmium.

7. A method according to claim 5, wherein said Group VI metal source is selected from the group consisting of dimethyl-, diethyl- and dibutyltellurium.

8. A method according to claim 5, wherein said transition metal magnetic ion source is tricarbonyl (methylcyclopentadienyl) manganese.

9. A method according to claim 8, wherein said tricarbonyl (methyl-cyclopentadienyl) manganese is provided from a source thereof via supply means maintained at a temperature sufficiently high to prevent condensation of said tricarbonyl (methylcyclopentadienyl) manganese is heated to a temperature of about 100° to about 150° C.

10. A method according to claim 9, wherein said temperature is at least 100° C.

11. A method according to claim 9, wherein said source of tricarbonyl (methyl-cyclopentadienyl) manganese is heated to a temperature of about 150° to about 150° C.

12. A method according to claim 1, wherein said carrier gas is H2.

13. A method according to claim 1, wherein said substrate is GaAs.
of the tricarbonyl (methyl-cyclopentadienyl) manganese.

26. A method according to claim 25, wherein the temperature is at least 100° C.

27. A method according to claim 25, wherein the source of tricarbonyl (methyl-cyclopentadienyl) manganese is heated to a temperature of about 100° to about 150° C.

28. A method according to claim 20, wherein the substrate is GaAs.

29. A method according to claim 28, wherein the substrate is (100) GaAs misoriented up to about 13° in a (110) or (111) direction.

30. A method according to claim 28, wherein the substrate is a CdS thin film.