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(54) Title: CHEMICAL VAPOR DEPOSITION FROM SINGLE ORGANOMETALLIC PRECURSORS
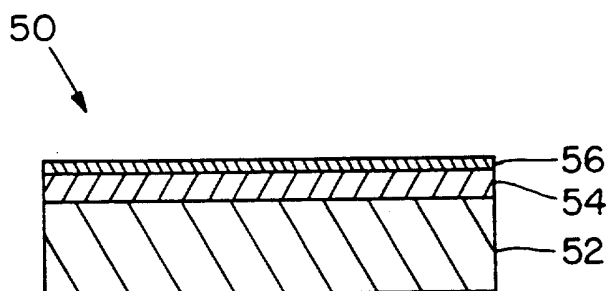
(57) Abstract

A method is disclosed for forming a passivating/buffer film on a substrate. The method includes heating the substrate to a temperature which is sufficient to cause a volatilized organometallic precursor to pyrolyze and thereby form a passivating/buffer film on a substrate (42). The organometallic precursor is volatilized at a precursor source (38). A carrier gas is directed from a carrier gas source (26) across the precursor source (38) to conduct the volatilized precursor from the precursor source (38) to the substrate (42). The volatilized precursor pyrolyzes and is deposited onto the substrate (42), thereby forming the passivating/buffer film on the substrate. The passivating/buffer film can be a cubic-phase passivating/buffer film. An oxide layer can also be formed on the passivating/buffer film to thereby form a composite of the substrate, the passivating/buffer film and the oxide layer. Cubic-phase passivating/buffer films formed by the method of the invention can be lattice-matched with the substrate. Electronic or electro-optical circuits or circuit elements can be formed which include passivating/buffer films formed by the method of the invention.

CHEMICAL VAPOR DEPOSITION FROM SINGLE
ORGANOMETALLIC PRECURSORS

Background of the Invention

Group 13-16 materials, and in particular, gallium
arsenide (GaAs), have been employed recently in an
increasing variety of electronic and electro-optical uses.
For example, integrated circuits which are based on active
layers of gallium arsenide, such as metal insulator
semiconductor field-effect transistors (MISFETs),
monolithic microwave integrated circuits (MMICs), and
fast-logic circuits, have been employed in digital signal
processing for military, biomedical, and communication-
systems applications. Gallium arsenide has also been
employed in the fabrication of minority charge-carrier
devices, such as solar cells and photodetectors. In
addition, optical sources, such as lasers and light-
emitting diodes (LEDs), have been developed which are of
Group 13-16 materials, such as GaAs for the lasant medium.

However, surface states of gallium arsenide provide
sites for non-radiative recombination. Therefore,
passivation is generally required to maintain the mobility
of charge carriers. Examples of known methods of
passivating gallium arsenide include deposition or growth
of oxides, nitrides or sulfides by various techniques,
such as molecular beam epitaxy (MBE), physical vapor
deposition (PVD), or electrochemical deposition.

Alternatively, buffer layers are enclosed to provide
an intermediate transitional layer between a semiconductor
substrate and subsequent layers to be formed over the
substrate. For example, high-resistance buffer layers
isolate circuits formed in active gallium arsenide layers
from the underlying substrate. See, for example, U.S.
Patent 4,952,527, issued August 28, 1990.

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There are several problems associated with known
methods of passivating gallium arsenide and with forming
buffer layers on gallium arsenide. For example, more than
one chemical precursor is typically required to form the
5   chemical compound deposited on gallium arsenide substrate.
Use of multiple precursors often causes formation of
impurities and consequent irregular composition of the
passivating/buffer layer by incorporation of impurities in
the passivation layer during deposition. Further, some
10   passivating/buffer layers, such as arsenic trisulfide,
which can be formed by known methods, are often toxic. In
addition, sulfurizing techniques generally form
passivating layers which are relatively unstable. Also,
known methods for deposition of passivating/buffer layers
15   often require exposure of the gallium arsenide substrate
to high temperatures, which can degrade the substrate. In
addition, there are other problems commonly associated
with known methods of deposition, such as slow deposition
rates, and the requirement of expensive, complicated
20   equipment for conducting deposition on gallium arsenide
substrates.

        Therefore, a need exists for an improved method for
forming a passivating/buffer films on gallium arsenide or
other semiconductor substrates, which overcome or minimize
25   the above-listed problems.

Summary of the Invention

        The present invention relates to a method for forming
a film on a substrate.

        The method includes heating the substrate to a
30   temperature sufficient to cause a volatilized precursor,

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which consists essentially of a single organometallic
compound, to pyrolyze the volatilized precursor and cause
the pyrolyzed precursor to be deposited on the substrate.
The precursor is volatilized at a precursor source. A
5   carrier gas from a carrier gas source is directed across
the precursor source to conduct the volatilized precursor
from the precursor source to the substrate, whereby the
volatilized precursor is pyrolyzed and is deposited onto
the substrate, thereby forming the film on the
10   substrate. The organometallic compound can be a cubane or
cubane-forming organometallic compound.

A composite material, formed by the method of the
invention, includes a substrate and a cubic-phase film.
The cubic-phase film includes a first component selected
15   from Group 13 of the Periodic Table and a second component
selected from Group 16 of the Periodic Table, wherein the
first and second components are arranged as face-centered
cubic-phase cells of a crystal structure.

In another embodiment, a composite, formed by the
20   method of the invention, includes a substrate, a cubic-
phase film which is formed on the substrate, and an oxide
layer formed on the cubic-phase film.

This invention has many advantages. For example, the
film is formed by metal-organic chemical vapor deposition
25   (MOCVD) from a single organometallic precursor. As a
consequence, no toxic impurities are contained within the
film. Further, a film having a substantially uniform
crystal structure is deposited, resulting in a
significantly reduced likelihood that defects will develop
30   in the film. Further, cubic-phase films are formed,
thereby enabling the formation of crystal structures which

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lattice-match the crystal structure of the substrate upon
which additional films can subsequently be formed.
Lattice-matching, in turn, further reduces the likelihood
that defects in the film will develop. Also, cubic-phase
5   films significantly enhance photoluminescence intensity by
reducing non-radiative recombination centers and by
reducing surface recombination velocity (SRV). In
addition, these cubic-phase films have a large band gap.
Therefore, the quality of electro-optical substrate
10 components, such as those formed of gallium arsenide, are
significantly increased. In addition, the cubic-phase
films can themselves be employed as semiconductors.
Further, the films which are formed by the method of the
invention are relatively stable. The films can be
15 passivating or buffer films. Also, the buffer films
formed by the method of the invention can be employed in
electronic or electro-optical components which include an
oxide, or insulation layer. For example, the buffer film
can be disposed between a substrate and an oxide layer.

20 Brief Description of the Drawings
        Figure 1 is a schematic representation of one
embodiment of a system which is suitable for depositing a
film on a substrate by the method of the invention.
        Figure 2 is a section view of one embodiment of a
25 composite of the invention.
        Figure 3 is a section view of another embodiment of a
composite of the invention.
        Figure 4 is a section view of still another
embodiment of a composite of the invention.

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Figure 5 is a section view of another embodiment of a composite of the invention.

Figure 6 is a section view of a transistor of the invention.

5   Figure 7 is a bright-field TEM image of an InS film formed by the method of the invention.

Figure 8 is a selected-area electron diffraction pattern of the InS film shown in Figure 3.

Figure 9 is a plot of an X-ray diffraction pattern
10   from $2\theta=5°-85°$ of a sample of GaS chemical vapor deposited on GaAs by the method of the invention, with {200} and {400} regions indicated.

Figure 10 is a plot of an X-ray diffraction pattern from $2\theta=65°-67°$ of the sample represented in Figure 4, of
15   GaS chemical vapor deposited on GaAs at about the {400} region.

Figure 11 is a histograph of photoluminescence intensity for samples of GaS which has been vapor deposited onto GaAs by the method of the invention.

20   Detailed Description of the Invention

The features and other details of the invention, either as steps of the invention or as combinations of parts of the invention, will now be more particularly described and pointed out in the claims. It will be
25   understood that the particular embodiments of the invention are shown by way of illustration and not as limitations of the invention. The principle features of the invention may be employed in various embodiments without departing from the scope of the invention.

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The method of the invention generally includes forming a film on a substrate from a single organometallic precursor. First, an organometallic precursor is volatilized at a precursor source. A carrier gas is then directed from a carrier gas source across the precursor source to conduct the volatilized organometallic precursor from the precursor source to the substrate. The volatilized organic precursor is pyrolyzed and the pyrolyzed precursor is deposited onto the substrate, thereby forming the film on the substrate.

The substrate can be formed of Group 13-16 materials, such as single-crystal gallium arsenide, which can be used to form semiconductor devices, such as FETs, semiconductor lasers or diode lasers. Thus, while the description herein may, at times, refer to semiconductor substrates, no such limitation on the scope of the invention is intended thereby. Further, although the films of the invention and the films formed by the method of the invention may be referred to as passivating/buffer films, it is to be understood the use of these films is not intended to be limited to such purposes.

System 10, shown in Figure 1, is one embodiment of a system which is suitable for conducting the method of the invention. System 10 includes housing 12 having first end 14 and second end 16. Inlet 18 is disposed at first end 14. Outlet 20 is disposed at second end 16. An example of a suitable housing is a laminar-flow hot-wall glass reactor. Alternatively, the system can include a suitable metal-organic vapor deposition reactor. An example of a suitable metal-organic vapor deposition reactor is disclosed in U.S. Patent 4,839,145, the teachings of which are incorporated herein by reference. Valve 22 is

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disposed at conduit 24, which extends between carrier gas
source 26 and inlet 18. Valve 28 is disposed at conduit
30, which extends between oxygen source 32 and inlet 18.
Valve 34 is disposed at conduit 36, which extends from
5   outlet 20.

Precursor source 38 is disposed within first end 14
of housing 12. Precursor heating element 40 is disposed
outside housing 12 at first end 14 and proximate to
precursor source 38. Precursor heating element 40 is
10 suitable for heating precursor at precursor source 38 in
an amount sufficient to volatilize precursor within first
end 14 of housing 12.

Substrate 42, onto which a passivating/buffer film
is to be formed by the method of the invention, is
15 disposed within second end 16 of housing 12. Substrate 42
includes upward surface 44, which is suitable for
deposition of a passivating/buffer film by the method of
the invention. Substrate 42 within housing 12 is suitable
for deposition of a passivating/buffer layer on upward
20 surface 42 by the method of the invention. Examples of
suitable semiconductor or electro-optical substrates
include gallium arsenide and indium phosphide substrates.
A suitable metal, such as aluminum or a compound thereof,
can be included in the crystal structure of substrate 42.
25 A particularly preferred substrate is gallium arsenide.

Heating plate 46 is disposed on the exterior of the
housing 12 at second end 16 and is proximate to substrate
42. Heating plate 46 is suitable for heating substrate 42
within second end 16 of housing 12 in an amount sufficient
30 to cause pyrolysis of volatilized precursor at second end
16 and consequent deposition of the pyrolyzed precursor

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onto upward surface 44 of substrate 42. Insulator 48 is disposed over housing 12 at second end 16.

Precursor at precursor source 38 is an organometallic compound. The organometallic compound includes at least
5   one element from Group 13 of the Periodic Table, and at least one element from Group 16 of the Periodic Table. In addition, the organometallic compound includes at least one butyl group. The butyl group is either a tertiary or a normal-type butyl group. In one embodiment, the
10   organometallic precursor is a compound which, upon pyrolysis and deposition upon substrate, will form an amorphous passivating/buffer layer. An example of such an organometallic precursor is $[(^tBu)GaS]_7$. The procedure for formation of $[(^tBu)GaS]_7$, can be found in Example I, shown
15   below.

Other examples of suitable organometallic compounds which can be employed by the method of the invention to form non-cubic buffer films, such as non-cubic crystalline passivating/buffer films, on s include $[(^nBu)InS]_x$ and
20   $[(^nBu)InSe]_x$, wherein x is in the range of between about four and eight; $[(^tBu)_2In(S^tBu)]_3$; and $[(^nBu)_2In(S^tBu)]_3$. The method by which $[(^nBu)InS]_x$, $[(^nBu)InSe]_x$ is formed can be found in Cowley et al., Angew. Chem. Int. Ed. Engl.,30(9):1143-1145 (1991), the teachings of which are
25   incorporated by reference, wherein indium is substituted for gallium. The method by which $[(^tBu)_2In(S^tBu)]_2$ and $[(^nBu)_2In(S^tBu)]_3$ can be formed is shown below in Example II. Still another organometallic compound which is suitable for forming an amorphous passivating/buffer on
30   substrate 42 by the method of the invention is

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[('Bu)$_2$Ga(S'Bu)]$_2$. The method by which this organometallic
precursor can be formed is described in Power _et al._,
Organometallics,11(3):1055-1060 (1992), the teachings of
which are incorporated herein by reference.

5   In another embodiment, the precursor at precursor
source 38 is a cubane or cubane-forming organometallic
precursor. Suitable cubane and cubane-forming
organometallic precursors are those which, when employed
in the method of the invention, will form a cubic-phase
10   passivating/buffer film on substrate 42. Cubic-phase
films, as term is employed herein, have a cubic-phase
crystal structure, such as a face-centered cubic-phase
crystal structure, or a cubic-like structure, such as a
tetragonal structure.

15   Cubane organometallic precursors are those which have
a cubane molecular structure. Examples of suitable cubane
organometallic precursors include [('Bu)GaS]$_4$, [('Bu)AlS]$_4$,
[('Bu)GaSe]$_4$, and [('Bu)GaTe]$_4$. The method by which these
cubane organometallic precursors can be formed is
20   described in: Cowley _et al._, _Angew. Chem. Int. Ed.
Engl.,30_(9):1143-1145 (1991); Power _et al._, _J. Chem. Soc.,
Chem. Comm.,11_315 (1991); and Power _et al._,
Organometallics,11 (3):1055-1060 (1992), the teachings of
all of which are incorporated herein by reference.

25   Cubane-forming organometallic precursors are those
which acquire a cubane molecular structure during
volatilization or pyrolysis according to the method of the
invention. An example of a suitable cubane-forming
organometallic precursor is [('Bu)GaS]$_6$. The method by

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which this cubane-forming organometallic precursor is
formed can be found in Example III, shown below.

Substrate heating plate 46 is heated in an amount
sufficient to heat substrate 42 in housing 12 to a

5   temperature which is sufficient to cause volatilized
precursor at second end 16 of housing to pyrolyze and
thereby be deposited upon upward surface 44 of substrate
42. In one embodiment, substrate 42 is heated to a
temperature in the range of between about 100° and 800°C.

10 Preferably, substrate 42 is heated to a temperature in the
range of between about 250°C and 550°C.

Precursor heating element 40 is heated to a
temperature which is sufficient to volatilize the
precursor at precursor source 38 within first end 14 of

15 housing 12. In one embodiment, precursor heating element
40 is heated to a temperature in the range of between
about 50°C and 250°C. Preferably, precursor heating
element 40 is heated to a temperature in the range of
between about 100°C and about 250°C. The precursor at

20 precursor source 38 is thereby volatilized at first end 14
of housing 12.

Valve 22 is opened and carrier gas is directed from
carrier gas source 26 through conduit 24 and inlet 18 of
housing 12. The carrier gas is substantially inert in the

25 presence of volatilized precursor within housing 12.
Examples of suitable carrier gases include argon,
hydrogen, nitrogen, etc. Carrier gas directed into
housing 12 is conducted within housing 12 from first end
14 to second end 14 of housing 12, and thereby directs

30 volatilized precursor at first end 14 to substrate 42 at
second end 16 of housing 12.

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Volatilized precursor at second end 16 of housing 12
is pyrolyzed by heat radiated from substrate 42, thereby
forming a pyrolyzed precursor which deposits onto upward
surface 44 of substrate 42. The pyrolyzed precursor is
5   allowed to collect on upward surface 44 of substrate 42
until the amount of the pyrolyzed precursor which has
accumulated is sufficient to enable formation of a
passivating/buffer film having a desired thickness. In
one embodiment, the thickness of the passivating/buffer
10 film to be formed is in the range of between about 100Å
and about 10,000Å. Preferably, the thickness of the
passivating/buffer layer to be formed is in the range of
between about 2,000Å and about 5,000Å.

When the desired amount of pyrolyzed precursor has
15 accumulated on upward surface 44 of substrate 42, the flow
of carrier gas from carrier gas source 26 into housing 12
is secured by closing valve 22. Also, precursor heating
element 40 is allowed to cool, thereby discontinuing
volatilization of precursor at precursor source 38.

20   In addition, substrate heating plate 46 is allowed to
cool, thereby allowing substrate 42 and the pyrolyzed
precursor on substrate 42 to also cool. In the embodiment
wherein an organometallic precursor is employed which is
not a cubane or cubane-forming organometallic precursor,
25 the passivating/buffer film which is formed on substrate
42 is an amorphous or non-cubic crystalline
passivating/buffer film. Alternatively, in the embodiment
wherein a cubane or cubane-forming metal organic precursor
is employed, the passivating/buffer film which forms on
30 substrate 42 is a cubic-phase passivating/buffer film.

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In a preferred embodiment, a semiconductor or electro-optical substrate and an organometallic precursor can be selected so that the passivating/buffer film has a crystal structure which is lattice-matched with the

5   crystal structure of the substrate. For example, in one embodiment, the substrate is gallium arsenide, and the organometallic precursor is [('Bu)GaS]$_4$, which is a cubane organometallic precursor. The [('Bu)GaS)]$_4$ forms a cubic-phase gallium sulfide passivating/buffer film on the

10 substrate. The cubic-phase gallium sulfide passivating/buffer film is lattice-matched with the gallium arsenide substrate. Another example of a combination of a substrate and a passivating/buffer film that is lattice-matched with the substrate includes a

15 buffer film of indium sulfide on a semiconductor or electro-optical substrate of indium phosphide.

In a particularly preferred embodiment, the passivating/buffer film formed on substrate 42 has an element in common with the crystal of substrate 42. For

20 example, a passivating/buffer film of gallium sulfide, on a substrate of gallium arsenide, includes gallium as an element which is common to both the passivating/buffer film and substrate 42.

An insulating layer can be formed on the

25 passivating/buffer film disposed on substrate 42. Examples of suitable insulating layers include oxides, silicides, borides and carbides. In one embodiment, valve 28 is opened and an oxygen-containing gas is directed from oxygenation source 32 through conduit 30 and inlet 18 into

30 housing 12. Examples of suitable oxygen-containing gases include oxygen gas (O_2), dinitrogen oxide (N_2O) and ozone (O_3). The oxygen-containing gas is conducted to second

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end 16 of housing 12 and to substrate 42. Exposure of the
passivating/buffer film to the oxygen-containing gas
causes a component of the passivating/buffer film at an
exposed surface of the passivating/buffer film to oxidize,
5   thereby forming an oxide layer on the passivating/buffer
film.

Composite 50, formed by the method of the invention,
is shown in Figure 2. Composite 50 includes substrate
52. Passivating/buffer film 54 is disposed on substrate
10   52. In one embodiment, passivating/buffer film 54 is a
cubic-phase passivating/buffer film. Passivating/buffer
film 54 includes a first component, selected from Group 13
of the Periodic Table, and a second component, selected
from Group 16 of the Periodic Table. Oxide layer 56 is
15   disposed on passivating/buffer film.

It is to be understood that, alternatively, other
types of layers/films can be formed on the
passivating/buffer film disposed on substrate 42.
Examples of suitable types of layers/films which can be
20   formed on the passivating/buffer film include
semiconductor, conductor and/or an additional
passivating/buffer films. The additional films can be
formed on the passivating/buffer film by known methods or
by the method of the invention. In one alternate
25   embodiment, shown in Figure 3, composite 58 includes
substrate 60, passivating/buffer film 62 formed on
substrate 60, and active film 64 formed on
passivating/buffer film 62. Active film 64 can be formed
selectively on passivating/buffer film 62. Examples of
30   suitable substrates include gallium arsenide and gallium
phoshide. Examples of suitable passivating/buffer films

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are those discussed above with reference to Figure 1.
Suitable active films 64 include, for example, gallium
arsenide, gallium phosphide, and gallium aluminum arsenide
(GaAlAs). Quantum wells of gallium arsenide and gallium
5   aluminum arsenide can also be included.

In another alternate embodiment, shown in Figure 4,
composite 64 includes substrate 66, passivating/buffer
film 68 formed on substrate 66, and conductor film 70
formed on passivating/buffer film 68. Conductor film 70
10   can be formed selectively on passivating/buffer film 68.
Examples of suitable conductor films include gold, silver
and aluminum. In still another embodiment, shown in
Figure 5, composite 72 includes substrate 74,
passivating/buffer film 76 formed on substrate 74, active
15   layer 78 formed on passivating/buffer film 76, and
conductor layer 80 formed on active layer 78. Active
layer 78 and conductor layer 80 can be formed selectively.

Electronic circuits can also be formed by the method
of the invention which employ the composites and
20   passivating/buffer films of the invention. For example,
field-effect transistor (FET) 82, shown in Figure 6,
includes substrate 84. Buffer film 86 is formed on
substrate 84 by the method of the invention. It is to be
understood that buffer film 86 can be a cubic-phase buffer
25   film which is comprised, for example, of gallium sulfide.
Next, active semiconductor layer 88 is formed on buffer
film 86 and on doped regions 87,89, respectively. Active
semiconductor layer 88 can be formed selectively on buffer
film 86, such as by photolithography, etching, etc. Next,
30   insulating film 90, comprised, for example, of alumina
(Al_2O_3), is formed selectively on active semiconductor
layer 88, such as by photolithography, etching, etc.

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Source, drain, and channel regions are formed in active
semiconductor layer 88, such as by ion beam doping of such
regions after gate region 95 is deposited on insulating
film 90. Passivating layer 92, formed, for example, of
5   gallium sulfide, is then formed over insulator film 90.
Electrical contacts and/or interconnectors 94 are formed
by etching openings to active semiconductor layer 88 and
selectively depositing metallization, thereby forming FET
82.

10   The invention will now be further and specifically
described by the following examples. All parts and
percentages are by weight unless otherwise stated.

Example I

        [('Bu)GaS]$_7$ was formed by refluxing ['Bu)GaS]$_4$ (1.0 g,
15   1.57 mmol) in hexane (50 mL) for 4 days. The resulting
solution was reduced to dryness under vacuum, leaving a
white solid. ^{1}H NMR indicated this to be a new species
containing only small amounts (<15%) of [('Bu)GaS]$_4$.
['BuGaS]$_7$ was obtained pure by fractional crystallization,
20   being more soluble in hexane than [('Bu)GaS]$_4$. Yield
0.79g, 80%. MS, m/z (EI, %) 1054 (7M$^+$ - 'Bu, 100%); (CI,
Isobutane, %) 1112 (7M$^+$, 25%), 1054 (7M$^+$ - 'Bu, 15%). IR
(Nujol): 1172(s), 1009(m), 941(w), 807(s), 660(w),
529(w), 510(w). NMR (C$_6$D$_6$): ^{1}H 1.27 [27H, s, C(C$\underline{H}_3$)$_3$],
25   1.23 [9H, s, C(C$\underline{H}_3$)$_3$], 1.19 [27H, s, C(C$\underline{H}_3$)$_3$]. ^{13}C 30.07
[$\underline{C}$(CH$_3$)$_3$], 30.01 [$\underline{C}$(CH$_3$)$_3$], 29.93 [$\underline{C}$(CH$_3$)$_3$], 29.21 [C($\underline{C}$H$_3$)$_3$],
27.74 [C($\underline{C}$H$_3$)$_3$], 27.48 [C($\underline{C}$H$_3$)$_3$].

        Melting points were determined in sealed capillaries
and are uncorrected. Thermogravimetric and differential

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thermal analysis were measured on a Seiko 200 TG/DTA
instrument. Mass spectra were recorded using a JEOL AX-
505H mass spectrometer and associated data system. An
electron beam energy of 70 eV was used for EI mass
5   spectra. Isobutane was used as a reagent gas for CI mass
spectra. All spectra were recorded at 1500 mass
resolution. Reported m/z values are for the predominant
ion within the isotope pattern for each signal. IR
spectra (4000-400 cm^{-1}) were recorded on a Nicolet 5ZDX-
10   FTIR spectrometer as Nujol mulls on KBr plates. ^{1}H and ^{13}C
NMR spectra (in C_6D_6 unless otherwise stated) were recorded
on a Bruker AM-500 spectrometer, and chemical shifts are
reported in parts per million relative to external $SiMe_4$
in $CDCl_3$. [(^{t}Bu)GaS]$_4$ was prepared according to the
15   following published procedures: Power et al., J. Chem.
Soc., Chem. Commun.: 1315 (1991); and Power et al.,
Organometallics, 11: 1055 (1992), the teachings of which
are incorporated herein by reference. All manipulations
were carried out under an atmosphere of dry nitrogen.
20   Solvents were distilled and degassed before use.

Example II

Synthesis of [(^{t}Bu)$_2$In(μ-S^{t}Bu)]$_2$ was performed as
follows: A pentane solution of tris-tert-butylindium
(4.03 g, 14.1 mmol) was added to an excess of tert-
25   butylthiol (ca. 3 cm^3) in pentane. The resulting solution
was stirred for 30 minutes at room temperature, after
which the solvent was removed in vacuo. Yield: 4.5 g,
100%. The product was hygroscopic and was stored under an
inert atmosphere. Mass spectrum: m/z (EI) 579 (2M$^+$-^{t}Bu),
30   465 (2M$^+$-3^{t}Bu). IR (cm^{-1}): 2946(m), 2925(m), 2893(w),
2858(w), 2828(s), 1460(s), 1361(m), 1261(m), 1151(s),

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1097(m, br), 1012(m), 805(s), 575(w). NMR (δ, C_6D_6): ^1H
1.50 [18 H, InC(C$\underline{H}_3$)$_3$], 1.37 [9 H, SC(C$\underline{H}_3$)$_3$]. ^{13}C 45.48
[S$\underline{C}$(CH$_3$)$_3$], 37.04 [SC($\underline{C}$H$_3$)$_3$], 32.71 [InC($\underline{C}$H$_3$)$_3$],
31.84[In$\underline{C}$(CH$_3$)$_3$]. Similarly, [(^nBu)$_2$In(S^tBu)]$_3$ can be formed

5   by employing the same method, but using tris-$\underline{n}$-butyl
indium.

    Thermogravimetric analyses were obtained on a Seiko
200 TG/DTA instrument using an argon carrier gas. Mass
spectra were obtained by using a JEOL AX-505H mass

10 spectrometer and associated data system. An electron beam
energy of 70 eV was used for EI mass spectra, with a mass
resolution of 1500. Reported m/z values are for the
predominant ion within the isotope pattern for each
signal. The IR spectrum (4000-400 cm^{-1}) was recorded on a

15 Nicolet 5ZDX-FTIR spectrometer as a KBr disk. ^1H and ^{13}C
NMR spectra were obtained on a Bruker AM-400 spectrometer,
and chemical shifts are reported relative to SiMe$_4$ in
CDCl$_3$. XPS were collected on a Surface Science
Instruments Spectrometer (Model SSX-100) with a

20 monochromatized AlKα source. The spectra were acquired
with a 50 eV pass energy and a 1000 μm spot size. All
samples were sputtered with 3 keV Argon ions prior to data
collection to remove adventitious carbon. All spectra
were charge referenced independently to graphitic carbon

25 (C$_{1s}$ = 284.8 ± 0.1 eV), and gold (Au$_{4f}$ = 84.0 ± 0.1 eV).
TEM was performed on a Phillips EM420 analytical electron
microscope operating at 120 kV.

    All manipulations were carried out under a nitrogen
atmosphere. Solvents were dried over sodium under

30 nitrogen, and degassed prior to use. ^tBuSH (Aldrich) was

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a commercial sample, and was used without further purification. In('Bu)$_3$ was prepared according to Bradley et al., Organometallics,7: 1112 (1988), the teachings of which are incorporated herein by reference.

5   Example III

[('Bu)GaS]$_6$ was formed by heating solid [('Bu)GaS(py)]$_3$ (1.0 g, 1.40 mmol) to ca. 200-220°C under vacuum (10^{-3} torr). A small quantity of [('Bu)GaS]$_4$ began to sublime after 15 minutes at this temperature, and condensed on
10   cooler parts of the flask. After about 1 hour, heating was stopped, and the contents allowed to cool to room temperature. ^{1}H NMR indicated that the non-sublimed material remaining consisted mainly of one new species with some [('Bu)GaS]$_4$ (ca. 15%) and [('Bu)GaS]$_8$ (ca. 30%)
15   also present. Some crystalline material was separated by hand, the crystals which were hexagonal in shape, and whose ^{1}H NMR indicated them to be the new species. Yield 0.2 g, 50%. mp 230 (subl.). MS, m/z (EI, %): 897 (6M$^+$-'Bu, 60%), 636 (4M$^+$, 35%), 579 (4M$^+$-'Bu, 100%). (CI, NH$_3$,
20   %): 970 (6M$^+$ +NH$_3$, 25%), 953 (6M$^+$, 30%), 897 (6M$^+$-'Bu, 15%). IR (Nujol): 1171(s), 1007(m), 941(w), 807(m), 722(w), 529(w). NMR (C$_6$D$_6$) ^{1}H 1.23 [s, C(C$\underline{H}_3$)$_3$]. Analytical procedure was the same as that described for Example I.
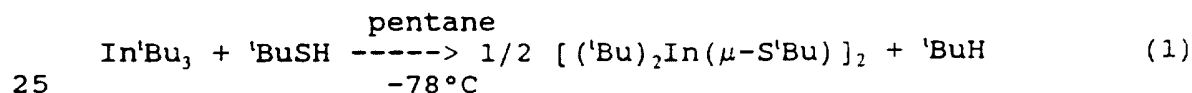
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Example IV
Deposition of Passivating/buffer Film

      Depositions were carried out in an atmospheric
pressure laminar-flow hot-wall glass reactor. Argon was
5   passed through a Cr/Cr_2O_3 gas purifier prior to entry into
the chamber. The CVD system was loaded with substrates
and purged for at least 2 hours prior to deposition,
during which time the hot zone was brought to the
deposition temperature (300-380°C). Outflow from the
10   reaction chamber exited to an oil bubbler, which prevented
back flow of air into the reaction chamber.
      Once the chamber was brought to the desired
temperature for deposition, approximately 500 mg of
$[({}^tBu)_2In(\mu-S^tBu)]_2$ was added and brought to a temperature
15   of 169-200°C. After each deposition, the films were
allowed to cool in the reactor under a flow of the carrier
gas. Deposition was carried out on a p-type (100)
oriented silicon wafers and KBr crystals.

Results of Deposition
20   The reaction of In^tBu_3 with one equivalent of ^tBuSH
yielded the dimeric thiolate compound $[({}^tBu)_2In(\mu-S^tBu)]_2$,
as shown below in Equation (1):

$$In^tBu_3 + {}^tBuSH \xrightarrow[-78°C]{pentane} 1/2\ [({}^tBu)_2In(\mu-S^tBu)]_2 + {}^tBuH \qquad (1)$$

25

    $[({}^tBu)_2In(\mu-S^tBu)]_2$ was characterized by ^1H and by ^{13}C
NMR, and IR spectroscopy. Thermogravimetric analyses were
obtained on a Seiko 200 TG/DTA instrument using an argon

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carrier gas. Mass spectra were obtained by using a JEOL
AX-505H mass spectrometer and associated data system. An
electron beam energy of 70 eV was used for EI mass
spectra, with a mass resolution of 1500. Reported m/z
5   values were for the predominant ion within the isotope
pattern for each signal. The IR spectrum (4000 -
400 cm⁻¹) was recorded on a Nicolet 5ZDX-FTIR spectrometer
as a KBr disk. ^1H and ^{13}C NMR spectra were obtained on a
Bruker AM-400 spectrometer, and chemical shifts were
10   reported relative to $SiMe_4$ in $CDCl_3$. XPS were collected on
a Surface Science Instruments Spectrometer (Model SSX-100)
with a monochromatized Al-Kα source. The spectra were
acquired with a 50 eV pass energy and a 1000 μm spot size.
All samples were sputtered with 3 keV Argon ions prior to
15   data collection to remove adventitious carbon. All
spectra were charge-referenced independently to graphitic
carbon (C_{1s} = 284.8 ± 0.1 eV), and gold (Au $4f^{7/2}$= 84.0 ±
0.1 eV). TEM was performed on a Phillips EM420 analytical
electron microscope operating at 120 kV.
20   All manipulations were carried out under a nitrogen
atmosphere. Solvents were dried over sodium under
nitrogen, and degassed prior to use. 'BuSH (Aldrich) was
a commercial sample, and was used without further
purification. In('Bu)₃ was prepared according to
25   literature Bradley et al., Organometallics,7: 1112 (1988)
the teachings of which are incorporated herein by
reference.
         The medium resolution EI mass spectrum indicated that
[('Bu)₂In(μ-S'Bu)]₂ existed as a thiolate-bridged dimer in
30   the gas phase, analogous to crystallographically-

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characterized thiolate compounds of aluminum (See Oliver
et al., Polyhedron,9:409 (1990), the teachings of which
ware incorporated herein by reference).

Thermogravimetric analysis (TGA) of [('Bu)$_2$In(μ-S^{t}Bu)]$_2$

5   were performed under an inert (dry N$_2$) atmosphere
displayed endotherms at ca.167°C, indicative of partial
sublimination of the dimer, followed by a weight loss and
exotherm at ca.224°C, consistent with the decomposition of
the molecule. Chemical vapor deposition (CVD) was

10 therefore performed operating within this sublimation -
decomposition 'window' by subliming the precursor at 169°C
into a horizontal-flow hot-walled chamber maintained at
atmospheric pressure, with deposition temperatures between
300-380°C. Deposition obtained by this method was found

15 to be very poor. Film thicknesses obtained after ca. 12
hours were non-uniform and estimated to be in the range of
3-4 nm, as evidenced by the presence of an attenuated
substrate signal by X-ray photoelectron spectroscopic
analysis, i.e., depth of XPS analysis is typically 3-5 nm.

20 Furthermore, substantial precursor decomposition was noted
with the initially white powder turning a mixture of
yellow, black and translucent materials. Sublimation with
no noticeable precursor decomposition was, however,
successfully enabled under vacuum (@10^{-3} Torr) at 60°C.

25   Deposited films were floated off KBr wafers and
analyzed by transmission electron microscopy (TEM).
Figure 3, the bright field image, showed the film to
consist primarily of uniform growth laths ca. 10 nm in
width. A defined set of trigonal growth directions (i.e.,

30 120° rotation) was visually identified in the (lighter)

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background or base layer in this film. This was reflected
in the selected-area electron diffraction pattern, Figure
4, where, despite the polycrystalline nature of the film,
a well-defined spot pattern indicative of preferred
5   orientation was obtained. The structure determined from
electron diffraction results was found to be the Hg_2Cl_2-
type tetragonal structure; consistent with the known high
pressure form of InS reported in Kabalkina et al., Solid
State Comm.,44:1383 (1982) the teachings of which are
10   incorporated by reference. EDX analysis indicated a film
composition of In:S to be 50:50 ($\pm 2\%$) in support of this
identification.

Example V

       Deposition of GaS was performed in a horizontal flow
15   hot-walled CVD chamber, as described above. A precursor,
[('Bu)GaS]$_4$, was sublimed at 760 torr at 225°C and
deposited using pre-dried argon as the carrier gas onto n-
type GaAs (undoped) and p-type GaAs substrates held at
390$\pm$10°C. Film thicknesses were estimated to be ~4000 -
20   5000 Å by comparison to Rutherford backscattering (RBS)
spectra of Si wafers coated alongside the GaAs substrates;
this was done to preclude damaging the GaAs samples by the
irradiation used for RBS. GaS had a high bandgap: the
films appeared clear when grown on glass substrates. GaS
25   also formed an excellent anti-reflective layer on GaAs
when grown to a suitable thickness.
       X-ray photoelectron spectroscopy (XPS) analysis
showed that the films were carbon- and oxygen-free beneath
the surface coverage of Ga_2O_3 and were GaS in composition:
30   the composition was confirmed by RBS, transmission
electron microscopic and energy dispersive x-ray analyses.

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Peak shifts for the Ga $2p^{3/2}$ were $2p^{1/2}$ were $105.3\pm0.2eV$ and $108.7\pm0.2eV$, respectively, vs. Au $4f^{7/2}=84$ eV reference.

Figure 5 shows the X-ray diffraction patterns of a typical GaS-coated GaAs substrate. Two prominent peaks
5 corresponding to d-spacings of 2.803 and 1.409 Å are evident. Although the underlying single-crystal GaAs would allow for reflections in these regions, {200} and {400} at 2.828 and 1.414 Å, respectively, a higher resolution scan, shown in Figure 6, around the {400}
10 reflection, reveals that this singlet is comprised of at least four component peaks. The peak at 1.414 Å may be attributed to the substrate GaAs {400} reflection attenuated by the GaS overlayer, as expected. The other peaks are most likely the {400} reflection of the GaS
15 coating displaying a range of d-spacings around an average value of 1.408 Å. The lattice parameter of this epitaxial GaS coating corresponds to a calculated cell constant of 5.63 Å.

The passivation of the GaS/GaAS interface was
20 evaluated by measuring the PLI before and after GaS deposition. The 514 nm line of an Ar+ laser at a power density of approximately $1W/cm^2$ was used for excitation. A large area silicon diode was employed to detect PL radiation from behind the sample. The details of the PLI
25 instrumentation are described in Jenkins, et al., Proc. 21st IEEE Photovoltaic Spec. Conf., Reno, NV, 1:399 (1990), the teachings of which are incorporated herein by reference. Figure 7a and Figure 7b show dramatic increases in the PLI of both p-type and n-type GaAs
30 samples, respectively. We observed less than 2% signal

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decay during experiments for periods exceeding one hour.
Pretreatment of the GaAs substrates was limited to oxide
removal in 50% HCl and drying under nitrogen.

The sharp increases in PLI indicated that surface
5   recombination velocity decreased and/or alteration of band
bending to reduce any front surface depletion region.
Cubic-phase GaS epitaxially grown at less than 400°C
formed stable passivating layers on both p- and n-type
GaAs. Photoluminescence measurements showed that the
10   interface exhibited a substantial decrease in surface
related-recombination and remained stable after 4 months.

Equivalents

Those skilled in the art will recognize, or be able
to ascertain using no more than routine experimentation,
15   many equivalents to the specific embodiments of the
invention described specifically herein. Such equivalents
are intended to be encompassed in the scope of the
following claims.

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CLAIMS

1. A method of forming a passivating film on a
    substrate, comprising the steps of:

    a)   heating the substrate to a temperature
5   sufficient to cause a volatilized precursor,
          which consists essentially of a single
          organometallic compound, to pyrolyze the
          volatilized precursor and cause the pyrolyzed
          precursor to be deposited on the substrate;
10   b)   volatilizing the precursor at a precursor
          source; and

    c)   directing a carrier gas from a carrier gas
          source across the precursor source to conduct
          the volatilized precursor from the precursor
15   source to the substrate, whereby the
          volatilized precursor is pyrolyzed and is
          deposited onto the substrate, thereby forming
          the passivating film on said substrate.

2.   The method of Claim 1, further including the step of
20   exposing the film to conditions sufficient to form
     an oxide of a component of the film, whereby an
     oxide layer is formed on the film.

3.   A method of significantly reducing the surface
     recombination velocity of a substrate, comprising
25   the steps of:

    a)   heating the substrate to a temperature
          sufficient to cause a volatilized precursor,
          which consists essentially of a cubane or
          cubane-forming organometallic compound, to
30   pyrolyze the volatilized precursor and cause

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the pyrolyzed precursor to be deposited on the
substrate;

b)   volatilizing the precursor at a precursor
source; and

5   c)   directing a carrier gas from a carrier gas
source across the precursor source to conduct
the volatilized precursor from the precursor
source to the substrate, whereby the
volatilized precursor is pyrolyzed and is

10   deposited onto the substrate to form a cubic
film on the substrate, thereby significantly
reducing the surface recombination velocity of
the substrate.

4.   A transistor, formed by a method comprising the

15   steps of: .

a)   forming a buffer film on a semiconductor
support by metal-organic chemical vapor
deposition and employing a single
organometallic precursor;

20   b)   forming an active layer on the buffer film;

c)   forming a circuit element in the active layer;

d)   forming a passivating film over the active
layer; and

e)   forming electrical contacts to the circuit

25   elmement in the active layer.

5.   A cubic-phase film, comprising:

a)   a first component selected from Group 13 of the
Periodic Table; and

b)   a second component selected from Group 16 of

30   the Periodic Table, wherein the first and

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second components are arranged as face-centered cubic-phase cells.

6.   The cubic-phase film of Claim 5, wherein the first component is gallium.

5 7.   The cubic-phase film of Claim 6, wherein the second component is sulphur.

8.   A composite material, comprising:
     a)   a substrate; and
     b)   a cubic-phase film, including
10   . i)   a first component selected from Group 13 of the Periodic Table, and
             ii) a second component selected from Group 16 of the Periodic Table, wherein the first and second components are arranged as
15   face-centered cubic-phase cells of a crystal structure.

9.   The composite material of Claim 8, wherein the substrate includes a component which is in common with the cubic-phase film.

20 10. The composite material of Claim 9 wherein the common component of the substrate and of the film is gallium.

11. The composite material of Claim 8 wherein the substrate includes gallium arsenide.

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12. A cubic-phase film, formed by a method comprising
    the steps of:

    a) heating the substrate to a temperature
        sufficient to cause a volatilized precursor,

5   which consists essentially of a cubane
        organometallic compound that includes at least
        one metal element in common with said
        substrate, to pyrolyze the volatilized
        precursor and cause the pyrolyzed precursor to

10   be deposited on the substrate as a film which
        can form a cubic-phase film;

    b) volatilizing the precursor at a precursor
        source; and

    c) directing a carrier gas from a carrier gas

15   source across the precursor source to conduct
        the volatilized precursor from the precursor
        source to the substrate, whereby the
        volatilized precursor is pyrolyzed and is
        deposited onto the substrate, thereby forming

20   the cubic-phase film on the substrate.

13. A composite material, formed by a method comprising
    the steps of:

    a) heating a substrate to a temperature sufficient
        to cause a volatilized precursor, which

25   consists essentially of a cubane or cubane-
        forming organometallic compound, to pyrolyze
        the volatilized precursor and cause the
        pyrolyzed precursor to be deposited on the
        substrate as a film which can form a cubic-

30   phase film;

    b) volatilizing the precursor at a precursor
        source; and

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 c) directing a carrier gas from a carrier gas source across the precursor source to conduct the volatilized precursor from the precursor source to the substrate, whereby the

5   volatilized precursor is pyrolyzed and is deposited onto the substrate, thereby forming the cubic-phase film on the substrate.

14. A method of forming a composite material of a substrate, a cubic-phase layer, and an oxide layer,

10 comprising the steps of:

 a) heating the substrate to a temperature sufficient to cause a volatilized precursor, which consists essentially of a cubane or cubane-forming organometallic compound, to

15   pyrolyze the volatilized precursor .and cause the pyrolyzed precursor to be deposited on the substrate as a film which can form a cubic-phase passivating/buffer film;

 b) volatilizing the precursor at a precursor

20 source;

 c) directing a carrier gas from a carrier gas source across the precursor source to conduct the volatilized precursor from the precursor source to the substrate, whereby the

25   volatilized precursor is pyrolyzed and is deposited onto the substrate, thereby forming the cubic-phase film on the substrate; and

 d) exposing the cubic-phase film to conditions sufficient to form an oxide of a component of

30   the film, whereby an oxide layer on the film is formed, thereby forming the composite materials.

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15. The method of Claim 14 wherein the oxidized
    component of the cubic-phase layer is common to the
    cubic-phase film and the substrate.

16. The method of Claim 15 wherein the element is common
5   to the cubic-phase film and the substrate is
    selected from Group 13 of the Periodic Table.

17. A composite, comprising:
    a)   a substrate;
    b)   a cubic-phase film disposed on the substrate;
10   and
    c)   an oxide layer disposed on the cubic-phase
         film.

18. The composite of Claim 17 wherein an element is
    common to the substrate, the cubic-phase film and
15 the oxide layer.

19. The composite of Claim 18 wherein the element
    common to the substrate, the cubic-phase film and
    the oxide layer is selected from Group 13 of the
    Periodic Table.

20 20. The composite of Claim 19 wherein said element is
    gallium.

21. The composite of Claim 19 wherein said element is
    aluminum.

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22. A device, comprising;
   a)   a semiconductor support;
   b)   a cubic-phase buffer film formed on the
        semiconductor support;
   c)   an active layer formed on the cubic-phase
        buffer film;
   d)   a circuit element formed in the active layer;
        and
   e)   at least one electrical contact to the circuit
        element in the active layer.

23. A composite comprising:
   a)   a substrate;
   b)   a cubic-phase film formed on the substrate; and
   c)   an active layer formed on the cubic-phase film.

24. The composite of Claim 23, further comprising a
    metal layer formed on the active layer.

25. A composite comprising:
   a)   a support;
   b)   a cubic-phase film formed on the substrate; and
   c)   an active layer formed on the cubic-phase film;
        and
   d)   a metal layer formed on the active layer.

26. The device of Claim 22 wherein the circuit element
    is an electrical or opto-electrical element.

27. The device of Claim 26 wherein the circuit element
    is a transistor.

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28. The device of Claim 22 wherein the circuit element
    is a field-effect transitor.

29. The device of Claim 22 further including a cubic-
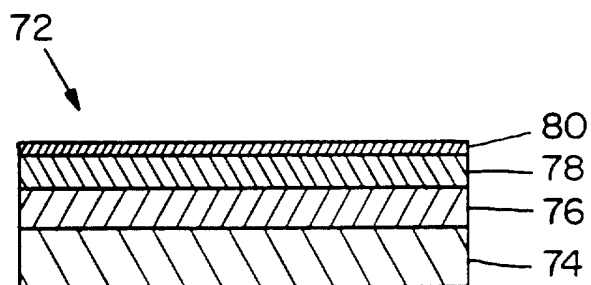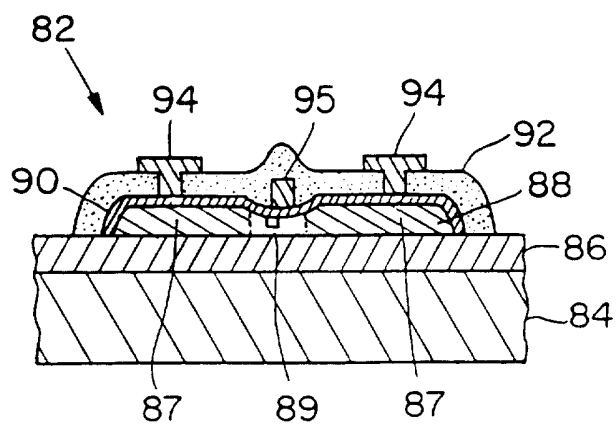   phase passivating film formed on the active layer.
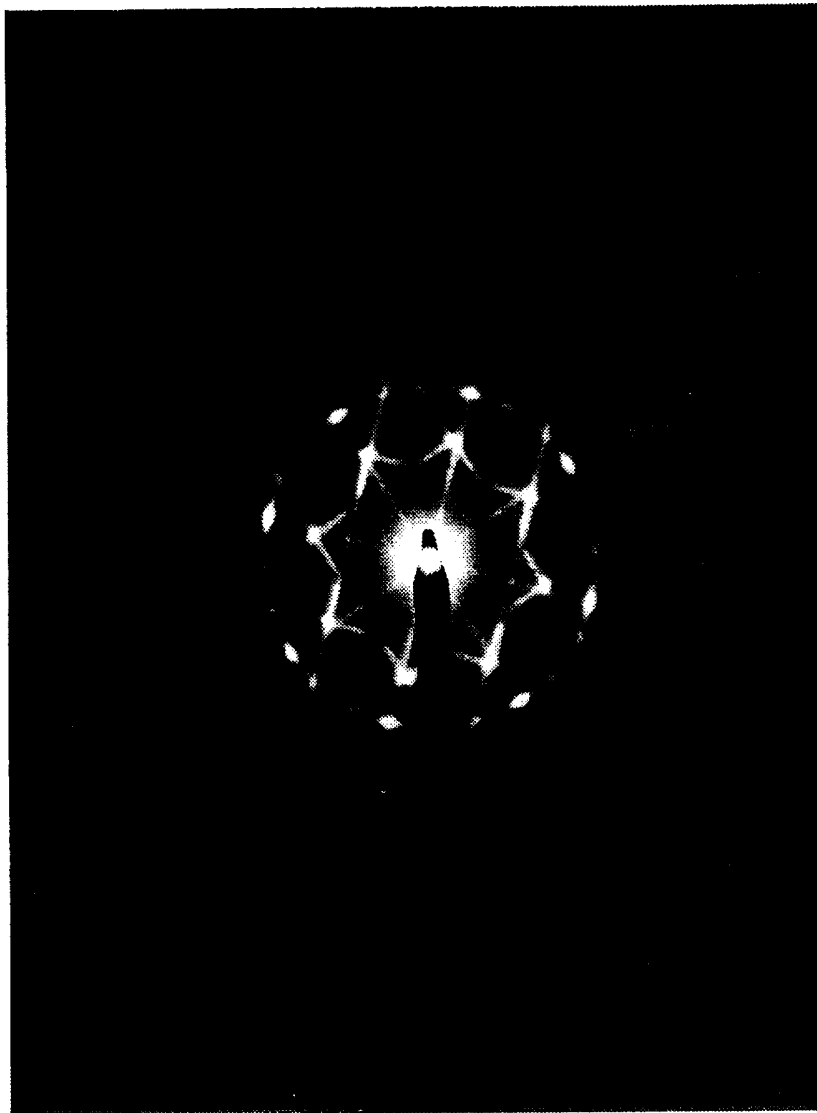
Fig. 1
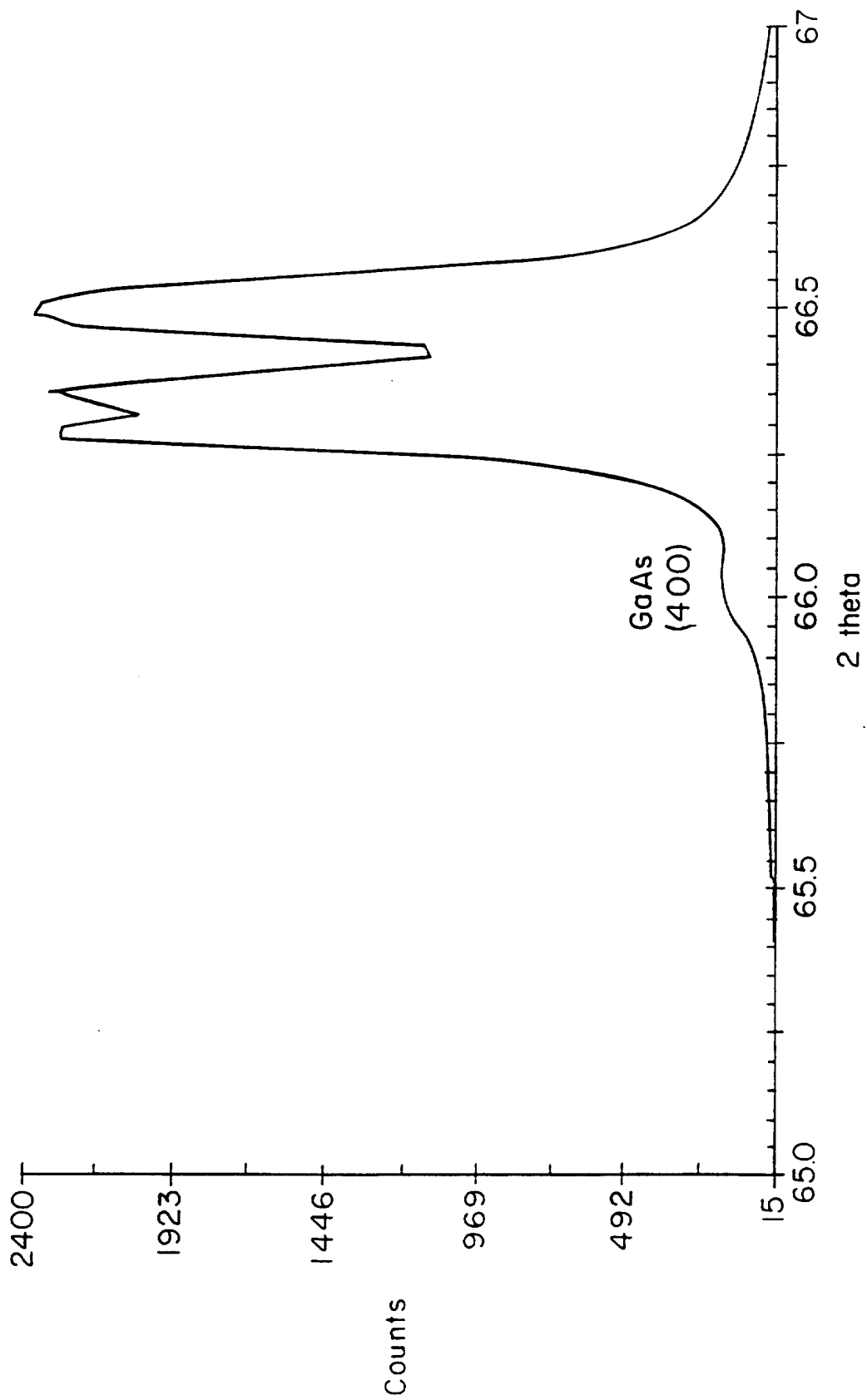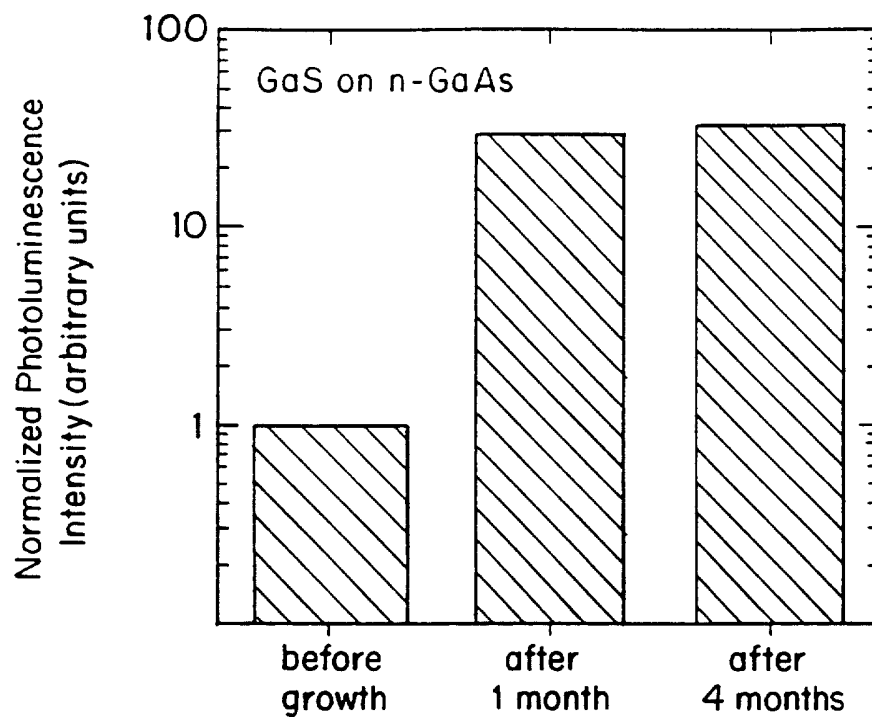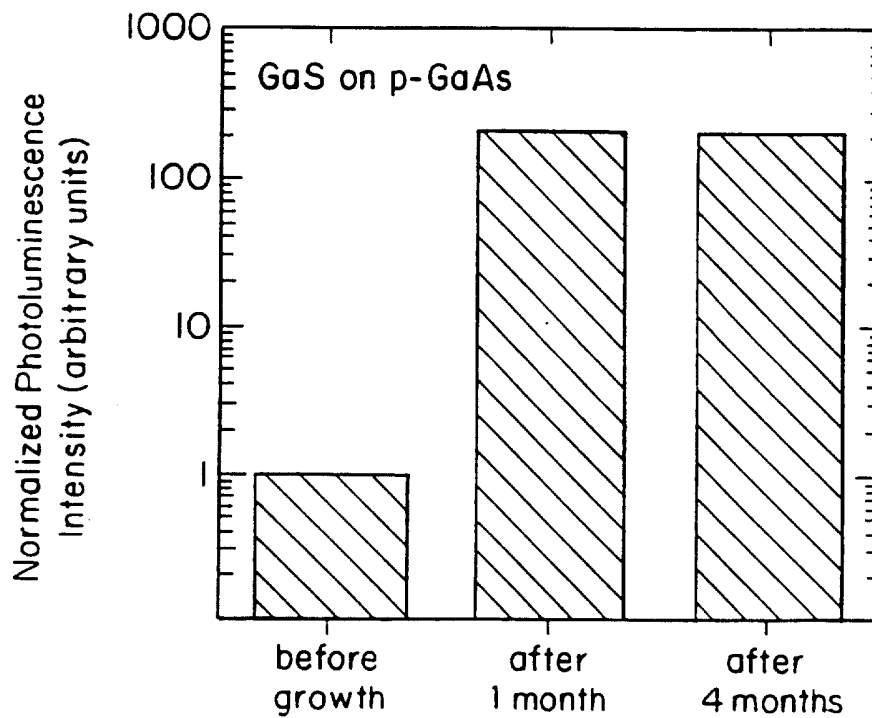

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig. 9

Fig. 10

Fig. 11a

Fig. 11b