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(54) Title: METHODS AND SYSTEMS FOR MONITORING AND CONTROLLING LAYER FORMATION USING P-POLARIZED REFLECTANCE SPECTROSCOPY

(57) Abstract

Formation of a layer on a substrate (16) is monitored by impinging P-polarized light on the layer during layer formation at approximately the Brewster's angle for the substrate, and detecting radiation (46) which is reflected from the structure. In heterostructure formation, an interference signal having a predetermined periodicity is monitored. Maxima and/or minima in the interference signal are monitored and an amplitude modulated fine signal which is superimposed on the interference signal is also monitored. The layer formation process is controlled based on the monitored interference signal, ratio of the maxima and/or minima, fine signal, fine signal amplitude modulation and/or combinations thereof by comparing the signals to a mathematical model or empirical data reference (84). A heterostructure formation or etching can also be used to calibrate a homostructure formation. Scattered light (48) may also be correlated to the reflected light to reduce the scattering component of the reflected light.

METHODS AND SYSTEMS FOR MONITORING AND CONTROLLING LAYER FORMATION USING P-POLARIZED REFLECTANCE SPECTROSCOPY

U.S. Government Rights

This invention was made with government support under Grant No. DMR-92-02210 awarded by the National Science Foundation. The U.S. Government has
5   certain rights in the invention.

Field of the Invention

This invention relates to layer formation methods and systems and more particularly to methods and systems for monitoring and controlling layer
10 formation.

Background of the Invention

Many techniques are used to form a layer on or in a substrate. For example, deposition, diffusion or etching may be used. Deposition and etching of a
15 layer (film) on a substrate are widely used processes in corrosion protection, antireflection coatings, enhanced surface hardness and wear resistance, as well as microelectronics and other fields of application. For example, microelectronic device manufacturing
20 typically requires deposition of one or more layers on a substrate. In some processes, a layer is deposited on a substrate of the same material to form a homostructure. In other operations, a layer is

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deposited on a substrate of a different material to form a heterostructure. Often, the layer and the substrate are monocrystalline, such that homoepitaxial deposition and heteroepitaxial deposition are

5   performed. However, amorphous or polycrystalline layers are also possible.

The layer to be deposited may be one or more single element semiconductors, compound semiconductors, metals, superconductors or dielectrics. Other

10 materials, such as ferroelectric materials may also be deposited. These depositions produce microelectronic devices such as semiconductor integrated circuit chips, optical devices, and thin film magnetic heads. Often, multiple layers are deposited on a substrate to form a

15 superlattice or other structure. Accordingly, a layer may be deposited directly on a substrate, or indirectly on a substrate by deposition on another layer which itself is formed directly or indirectly on a substrate. Similar considerations and terminology apply to etching

20 processes.

Deposition and etching processes require *in situ*, real-time monitoring of the growth or shrinkage of the layer which is deposited or etched on the substrate. For example, as the integration density of

25 microelectronic devices continues to increase, and new and exotic materials are introduced into microelectronic manufacturing methods, the monitoring and controlling of deposition and etching becomes even more critical, so that the layer has the desired

30 thickness and the desired electrical, optical and other properties.

Many techniques have been developed to monitor and control deposition. For example, Reflection High Energy Electron Diffraction (RHEED) has

35 been developed to monitor the intensity of diffracted electron beams projected across a substrate face.

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RHEED has allowed atomic layer controllability of initial epitaxial growth.

Some of these techniques involve optical detection because optical detection is nondestructive
5 of the layer being deposited. For example, Surface Photo Absorption (SPA) has been used to monitor the initial growth of a homoepitaxial layer. In this technique, linearly polarized radiation, whose polarization **E** vector is perpendicular to the substrate
10 surface (i.e. P-polarized) and whose energy $(E=h\upsilon)$ exceeds the energy gap of the semiconductor being monitored, irradiates a (001)-oriented GaAs substrate at a shallow incidence angle of 70°. This is close to the Brewster's angle. The wavelength is selected to
15 lie in the high absorption region to obtain high surface sensitivity. The change in reflection intensity is explained by the absorption of incident light by the surface chemical species.

Many publications describe the use of SPA to
20 measure initial growth of a homoepitaxial deposition of gallium arsenide on a gallium arsenide substrate. See, for example, Horikoshi, Yoshiji, *"Epitaxial Growth of III-V Compound Semiconductor Thin Films and Their Device Applications"*, Prog. Crystal Growth and
25 Charact., Vol. 23, 1991, pp. 73-126; Kobayashi, Naoki, et al., *"Spectral Dependence of Optical Reflection during Flow-Rate Modulation Epitaxy of GaAs by the Surface Photo-Absorption Method"*, Japanese Journal of Applied Physics, Vol. 29, No. 5, May 1990, pp. L702-
30 L705; Kobayashi, N., et al. *"In-situ monitoring of GaAs growth process in MOVPE by surface photo-absorption method"*, Journal of Crystal Growth, Vol. 107, 1991, pp. 62-67; Horikoshi, Yoshiji, et al., *"Optical investigation of GaAs growth process in molecular beam*
35 *epitaxy and migration-enhanced epitaxy"*, Journal of Crystal Growth, Vol. 111, 1991, pp. 200-204; Kobayashi, Naoki, et al., *"In-situ monitoring and control of*

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atomic layer epitaxy by surface photo-absorption", Thin
Solid Films, Vol 225, 1993, pp. 32-39; Kobayashi,
Naoki, et al., *"Optical Investigation on the Growth
Process of GaAs during Migration-Enhanced Epitaxy"*,

5   Japanese Journal of Applied Physics, Vol. 28, No. 11,
November 1989, pp. L1880-L1882; Kobayashi, Naoki, et
al., *"Investigation of Growth Processes in Flow-Rate
Modulation Epitaxy and Atomic Layer Epitaxy by New In-
Situ Optical Monitoring Method"*, citation unknown,

10   1990, pp. 139-145; Yamauchi, Yoshiharu, et al., *"In
Situ Spectrum Observation of Ga Deposition Process
during GaAs Metal-Organic Chemical Vapor Deposition
Using Surface Photo-Absorption"*, Jpn. J. Appl. Phys.,
Vol. 32, Part. 2, No. 10A, 1 October 1993, pp. L1380-

15   L1392; Uwai, Kunihiko, et al., *"Arsenic Coverages and
Surface Structures of As-Stabilized GaAs (001) Surfaces
during Metalorganic Chemical Vapor Deposition Observed
by Reflectance Difference"*, Jpn. J. Appl. Phys., Vol.
32, Part 1, No. 12A, December 1993, pp. 5479-5486;

20   Yamauchi, Yoshiharu, et al., *"Spectral Observation of
As-Stabilized GaAs Surfaces in Metal-Organic Chemical
Vapor Deposition Using Surface Photo-Absorption"*, Jpn.
J. Appl. Phys. Vol. 32, Part 1, No. 8, August 1993, pp.
3363-3369; Yamauchi, Yoshiharu, et al., *"Decomposition

25   of Arsine and Trimethylarsenic on GaAs Investigated by
Surface Photo-Absorption"*, Japanese Journal of Applied
Physics, Vol. 29, No. 8, August 1990, pp. L1353-L1356;
Makimoto, Toshiki, et al., *"In Situ Optical Monitoring
of the GaAs Growth Process in MOCVD"*, Japanese Journal

30   of Applied Physics, Vol. 29, No. 2, February 1990, pp.
L207-L209; Simko, J.P., et al., *"Surface photo-
absorption study of the laser-assisted atomic layer
epitaxial growth process of GaAs"*, Thin Solid Films,
Vol. 225, 1993, pp. 40-46; and Zama, Hideaki, et al.,

35   *"In Situ Monitoring of Optical Reflectance Oscillation
in Layer-by-Layer Chemical Vapor Deposition of Oxide
Superconductor Films"*, Jpn. J. Appl. Phys., Vol. 31,

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Pt. 2, No. 9A, 1992, pp. 1243-1245. See also, Japanese
patent application 3-174739 to Kobayashi, et al.,
published on July 29, 1991.

Coinventor Dietz and H. J. Lewerenz also
5 developed a technique referred to as Brewster's Angle
Reflective Spectroscopy (BARS) which is based on the
changes of reflectivity of P-polarized light at the
substrate Brewster's angle. BARS works at precisely
the Brewster's angle of the material being tested. It
10 detects interference oscillations in reflected light
intensity and thus is theoretically predicted to
measure layer thickness. Changes in the reflectivity
are large enough to monitor layer growth as well as to
reveal the thin film thickness and optical constants of
15 the film. See the publication by Dietz, N., et al.,
entitled "An optical in-situ method for layer growth
characterization", Applied Surface Science, Vol. 69,
1993, pp. 350-354.

The above-described RHEED and SPA techniques
20 are highly sensitive during the initial atomic
monolayers of growth. Unfortunately, RHEED loses
sensitivity over the entire duration of the growth
process. SPA works at energies where the sample under
test is strongly absorbing, thus preventing penetration
25 of the light into the bulk of the film being deposited.
Consequently, SPA only probes surface properties. SPA
does not allow a correlation of the surface induced
signal to the bulk properties of the layer, including
its thickness. BARS theoretically predicts that
30 interference oscillations in reflected light intensity
can measure film thickness, but does not predict other
useful monitoring and control information can be
obtained from the interference oscillations.

Other techniques may also be used to form
35 layers on or in a substrate. Diffusive film formation
may be used to diffuse materials into a substrate to
form a layer therein. For example, in microelectronic

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diffusive film formation techniques, zinc and
phosphorus may be diffused into a silicon substrate to
form a surface layer of $ZnSiP_2$ therein. See for example
the publication by G.K. Averkieva et al. entitled
5   *"Prospects for Using $A^{II}/B^{IV}/C_2^V$ Semiconductors in
Heterojunctions with Silicon"*, Izvestiya Akademii Nauk
SSSR, Neoorganicheskie Materialy, Vol. 19, No. 12,
pages 1967-72, December 1983. Diffusive film
consumption may also be used. For example, a
10   refractory metal film may be deposited directly on a
silicon substrate surface, and the substrate is heated
so that the metal and silicon react to form a silicide.
During this process, at least some of the silicon
substrate is typically consumed during conversion into
15   silicide. A self-aligned silicide process, known as a
SALICIDE process, is widely used for forming
interconnects on semiconductor substrates. As was
described above with respect to deposition or etching,
in situ, real time monitoring is also required for
20   these layer forming processes.
        Monitoring of layer formation is not limited
to microelectronics. For example, in the study of
immunological and enzymatic reactions on a solid
surface, it is known to use plane-polarized light to
25   optically monitor these reactions. See the publication
entitled *"Reflectometry in Kinetic Studies of
Immunological and Enzymatic Reactions on Solid
Surfaces"* by Welin et al., Analytica Chimica Acta, 163
(1984), pp. 263-267. See also the publication by Arwin
30   et al. entitled *"A Reflectance Method for
Quantification of Immunological Reactions on Surfaces"*,
An Optical Method for Immunology, Academic Press, Inc.,
1985, pp. 106-112. In these processes, it is also
important to monitor the layer formation, so as to
35   monitor periodic chemical/biological surface processes.

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Summary of the Invention

It is therefore an object of the invention to provide improved methods and systems for monitoring and controlling formation of a layer on or in a substrate.

5   It is another object of the present invention to provide methods and systems for monitoring and controlling layer formation during the initial monolayers of formation and during the entire layer formation.

10   It is yet another object of the present invention to provide methods and systems for monitoring and controlling layer formation which provide data concerning overall layer thickness, as well as data concerning the quality of the formed layer.

15   These and other objects are provided, according to the present invention, by systems and methods for monitoring formation of a layer on or in a substrate to form a heterostructure, for example by deposition or etching wherein polarized radiation is

20   impinged on the layer during deposition or etching thereof at an angle which is approximately the Brewster's angle for the substrate or of the formed layer (i.e. within approximately ±10° of the Brewster's angle), and radiation which is reflected from the

25   heterostructure is detected to produce an interference signal having a predetermined periodicity. Various components of the interference signal are monitored during the layer formation process to monitor formation of the layer, including the quality of the layer. For

30   purposes of the description which follows, reference will be made to the specific example of deposition or etching; however, it will be understood that any layer forming process is contemplated.

According to one aspect of the invention,

35   extrema (maxima and/or minima) in the interference signal are detected and a ratio of predetermined extrema is formulated in order to monitor deposition or

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etching of the layer including the properties thereof.
According to another aspect of the invention, a fine
signal which is superimposed on the interference
signal, and which has periodicity which is
5   substantially higher than the predetermined
periodicity, is monitored. According to both of the
above aspects, the deposition or etching process is
controlled based upon the monitored ratio of the
extrema, fine signal and combinations thereof, by
10 comparing the signals to reference signals derived from
mathematical models or empirical data, and controlling
the deposition or etching parameters when the monitored
signals deviate from the reference signals.
            According to another aspect of the invention,
15 it has been discovered that in a deposition or etching
process which involves pulsing of at least one
precursor or etchant of the layer at a predetermined
periodicity to deposit the layer on the substrate, the
detected radiation which is reflected from the
20 structure produces an amplitude modulated signal having
the predetermined periodicity. The amplitude
modulation of the amplitude modulated signal is
monitored to monitor and control the deposition,
diffusive formation or etching of the layer. Amplitude
25 modulation takes place during heteroepitaxial
deposition or etching, in which the fine signal which
is superimposed on the interference signal is amplitude
modulated, and during homoepitaxial deposition or
etching in which the fine signal itself is amplitude
30 modulated.
            For example, the fine structure superimposed
on the interference oscillation contains an
interference oscillation-related amplitude modulation
which is related to a periodic alternation of the
35 optical signal between a three component stack
(ambient/layer/substrate) and a four component stack
(ambient/surface reaction layer/layer/substrate). This

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periodic alteration results in periodic minima and
maxima in the fine structure with respect to the minima
and maxima in the interference oscillation. The
location of the minima and maxima of the amplitude
5   modulation of the fine signal relative to the minimum
and maximum of the interference signal can be detected.
These locations can be used to precisely measure the
imaginary part of the dielectric constant of the
surface reaction layer.

10   Moreover, the transients in the rising and
falling flanks of the fine structure can be utilized to
measure the overall surface reaction kinetics of the
deposition/diffusion or etching process of the material
systems.

15   According to yet another aspect of the
present invention, a heterodeposition or etching
process can be used to calibrate a homodeposition or
etching process. For example, a heterodeposition is
first performed and Brewster's angle reflectance
20   measurement signals are obtained to produce an
interference signal having a predetermined periodicity.
This interference signal having a predetermined
periodicity is used to calibrate a heterodeposition.
During the heterodeposition, a fine signal is produced
25   which has a periodicity which is substantially higher
than the predetermined periodicity. The deposition
rate associated with each peak of this superimposed
amplitude modulated fine signal is determined by
counting the numbers of peaks of the fine signal per
30   interference oscillation. In a homoepitaxial process
using the same deposition parameters as in the
preceding heteroepitaxial deposition process, the same
amplitude-modulated fine structure is observed.
However, an interference signal is not produced due to
35   the lack of an interface during homodeposition. The
fine signal is calibrated using the predetermined
periodicity, so that film growth in addition to the

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fine structure of film growth can be monitored and controlled. A heteroetching process is also used to calibrate a homoetching process in a similar manner.

   It has also been discovered that the detected
5 radiation which is reflected from the structure during deposition will contain a component that is a function of scattering rather than reflection. The scattered light is produced because of surface roughness of the growing layer and interface scattering. According to
10 another aspect of the invention, scattered radiation is also detected and is correlated with the reflected signal to produce a signal. For example, the scattered radiation signal is subtracted from the reflected signal to produce a signal which has a reduced
15 scattering component relative to the reflected signal. The reduced scattering component signal is monitored during deposition, for increased accuracy. Scattered radiation can be detected and correlated in an etching process in a similar manner.
20   The invention allows deposition and etching to be monitored and controlled during initial growth stages and continued growth stages by monitoring various signals which are obtained from radiation which is reflected from a substrate as a result of Brewster's
25 angle impingement of polarized radiation. The Brewster's angle of the substrate or the layer can be used, depending upon the parameters to be measured. A high degree of process control of bulk, interface and surface properties is thereby obtained to satisfy the
30 needs of state of the art manufacturing.

Brief Description of the Drawings

   Figure 1 illustrates a schematic view of a system for monitoring and controlling deposition according to the present invention.

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Figure 2 graphically illustrates a reflected radiation signal and a scattered radiation signal for a heterodeposition according to the present invention.

Figures 3A and Figure 3B graphically
5   illustrate a precursor pulse sequence and the corresponding fine signal structure respectively according to the present invention.

Figure 4 graphically illustrates amplitude modulation of the fine signal structure of a reflected
10 radiation signal according to the present invention.

Figure 5 graphically illustrates a reflected radiation signal and a scattered radiation signal for a homodeposition according to the present invention.

Figure 6 graphically illustrates detection of
15 the imaginary part of the dielectric function from the turning points in the amplitude modulated fine structure.

Figure 7 graphically illustrates an enlargement of the fine structure of Figure 6 adjacent
20 the minimum of the interference signal.

Figures 8A-8D graphically illustrate measurements of rise and fall times relative to precursor cycle sequences in order to obtain information concerning the surface kinetics of the
25 system.

Detailed Description of Preferred Embodiments

The present invention now will be described more fully hereinafter with reference to the accompanying drawings, in which preferred embodiments
30 of the invention are shown. This invention may, however, be embodied in many different forms and should not be construed as limited to the embodiments set forth herein; rather, these embodiments are provided so that this disclosure will be thorough and complete, and
35 will fully convey the scope of the invention to those skilled in the art. In the drawings, the thickness of

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layers and regions are exaggerated for clarity. Like
numbers refer to like elements throughout.

　　　　Referring now to Figure 1, a schematic view
of a system for monitoring and controlling deposition
5　using P-Polarized Reflective Spectroscopy (P-PRS) is
illustrated. System 10 includes a deposition chamber
12 having a substrate holder 14 therein for holding a
substrate 16 thereon. It will be understood by those
having skill in the art that substrate 16 can be a
10　silicon or other monocrystalline semiconductor
substrate, an optical substrate, or any other kind of
solid substrate. A substrate heater 18 may be provided
and a linear or rotational motion unit 22 may also be
provided to rotate, tilt and move the substrate 16 as
15　necessary. A bias current may also be provided to
substrate 16 through current feedthrough 24. An
electron gun 26, a RHEED screen 28 and a RHEED detector
32 provide an *in situ* RHEED monitoring system.

　　　　The description of system 10 will now
20　continue with a description of a system for monitoring
and controlling gallium phosphide (GaP) deposition on a
(001) silicon (Si) substrate by Pulsed Chemical Beam
Epitaxy (PCBE). However, this example is merely
illustrative, and other layers may be deposited or
25　etched on substrates under varying deposition and
etching conditions. It will also be understood that
other well known layer forming processes, including but
not limited to diffusive film formation, diffusive film
consumption, diffusive surface modification and
30　enzymatic or other biological reactions, may be
monitored and controlled.

　　　　Continuing with the description of Figure 1,
radiation is directed from a radiation source 34 to the
substrate 16 at an angle within about ±10° of
35　Brewster's angle φ. In the embodiment described,
radiation source 34 is a helium neon laser with a
wavelength of 6328Å, which is below the band gap of

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GaP. The coherent radiation is chopped by a chopper 36
and is P-polarized by a polarizer 38, for example a
Glan-Thompson prism with an extinction ratio better
than 10^6 for the P-polarized component. This generates
5 a P-polarized light beam of 632.8 nm. The radiation
irradiates the silicon surface at an angle of incidence
φ equal to 71° which is close to the Brewster's angle
of the substrate (about 75°). The angle of incidence
can be adjusted in the range of about ±5° to
10 synchronize the RHEED geometry conditions with the P-
polarized reflectance spectroscopy measurements. It
will be understood that the Brewster's angle of the
layer, rather than the Brewster's angle of the
substrate, may be used in order to better detect
15 surface phenomena in the layer during heteroepitaxial
growth.

The parallel polarized light is reflected
from the substrate 16 and detected by a reflected light
detecting unit 42 such as a silicon photodiode with an
20 integrated preamplifier. Simultaneously, the scattered
light component is detected using a scattered light
detecting unit 44, such as a sensitive photomultiplier
tube. It will be understood that incoherent radiation
can also be used.

25 The reflected radiation signal 46, the
scattered radiation signal 48 and the RHEED signal 52
are supplied to a controlling unit 54. It will be
understood by those having skill in the art that
controlling unit 54 may include specialized hardware, a
30 general purpose computer running a stored program, or
combinations thereof. It will also be understood that
signals 46, 48 and 52 may be buffered, amplified and/or
scaled prior to input into the controlling unit 54.

Still referring to Figure 1, first and second
35 precursor gas fluxes 62 and 64 are directed from first
and second precursor gas sources 56 and 58
respectively, into chamber 12 via computer controlled

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three-way valves 66 and 68 respectively, or other gas
control mechanisms. Valves 66 and 68 direct precursor
gases 62 and 64 respectively from sources 56 and 58
respectively into chamber 12 via inlets 72, 74
5   respectively, or to a separately pumped bypass chamber
(not illustrated). Sequential exposure of the
substrate to individual pulses of the precursor
molecules is thereby obtained. As will be described
below, the valves 66 and 68 may be controlled by
10 controlling unit 54.

For example, to deposit gallium phosphide,
the precursors used are triethylgallium (TEG) and
tertiarybutyl phosphine (TBP) in a hydrogen ambient.
The hydrogen scavenges organic molecules formed on the
15 surface of the layer due to pyrolysis of the TEG and
TBP molecules. The time constant of the system is
limited due to the response time of the switching
valves which is on the order of 0.2 seconds. Total gas
flow rate in chamber 12 is about 1 to 5 sccm which
20 leads to a pressure in the 10^{-5} to low 10^{-4} mbar during
the deposition. The substrate temperature is between
300-350°C. As will be described below, the switching
of the valves 66, 68 is synchronized with the data
acquisition of the reflected radiation signal to relate
25 observed changes in the reflected intensity of the
light with the vicinity surface chemistry induced
changes in the optical properties.

Controlling unit 54 includes signal
processing means 82 which processes the RHEED signal
30 52, the scattered radiation signal 48 and various
components of the reflected radiation signal 46. Among
the components of the reflected radiation signal 46
which are detected and processed by signal processing
unit 82, are an interference signal (heterodeposition
35 only), a ratio of extrema of the interference signal
(heterodeposition only), the fine structure of the
reflected radiation signal (hetero- and homodeposition)

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and amplitude modulation of the fine structure (hetero-
and homodeposition). The signals are processed by
signal processing means **82** as described below.

Once processed, comparing means **84** compares
5   the results to reference signals or parameters. The
references may be empirically derived from a reference
deposition process, may be theoretically derived using
the mathematical equations which govern the deposition
process, numerical modelling or combinations thereof.
10   Differences between the reference and the detected
signals are used to generate control signals in control
signal generating means **86** to control operation of
valves **66** and **68** and thereby control the deposition
process. It will be understood by those having skill
15   in the art that other components of system **10** may also
be controlled, in addition to or instead of valves **66**
and **68**. It will also be understood that one or more of
the processing, comparing and control signal generating
functions may be performed manually.
20   A detailed description of scattered radiation
signal **48** and reflected radiation signal **46** will now be
provided, along with a detailed description of the
operation of controlling unit **54** for processing these
signals and generating control signals based thereon.
25   The reflected radiation signal **46** contains
several components which can be divided into bulk and
surface vicinity related contributions to the
properties. The contribution related to the
heteroepitaxial growth of a layer is described by the
30   Fresnel equations for a three component system
(ambient/film/substrate). The changes in the amplitude
of the reflectance due to growth of a GaP layer were
predicted on the order of two to three orders of
magnitude with an interference periodicity of about
35   1060Å for a He-Ne laser (6328Å), assuming an angle of
incidence of $\varphi = 75.637°$ and dielectric constants of

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$\epsilon_{GaP} = (9.95, 0)$ and $\epsilon_{Si} = (15.25, 0.17)$ for GaP and Si, respectively.

The changes in the amplitude of the reflected P-polarized light beam depend strongly on the
5   differences in the dielectric functions of the grown layer and the underlying substrate, respectively. In the case of homoepitaxial film growth, the bulk/film related contribution in the reflected radiation signal vanishes, so that no information over the bulk
10   properties of the growing film are available presupposing identical substrate and film properties with an ideal interface. Only the near-surface contribution to the reflected radiation signal can be still observed, which is related to the surface
15   chemistry induced changes in the dielectric function within the first few monolayers of the growing layer, and interface related phenomena such as a non-ideal interface or chemical reaction of another species with the interface. This contribution can be maintained
20   throughout the entire layer growth.

The experimental results of heteroepitaxial growth of GaP on Si are graphically shown in Figure 2. The reflected intensity shows the gross interference oscillation 102, which is used to terminate the growth
25   of the film as soon as the reflected intensity reaches the second minimum. This corresponds to a film thickness of 1700Å±50Å, confirmed by Detak measurements. The error in the thickness is due to the lack of knowledge of the exact value of the angle of
30   incidence and the error in pinpointing the position of the second minimum, which presently relies on a visual inspection of the signal. These errors can be reduced or eliminated by comparison of the experimental data with theoretical model calculations, which can be used
35   to compute the optical constants of the growing layer as well as the deviations in the dielectric function

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during the growth and an accurate prediction of the
position of the minima.

Also shown in Figure 2, at **104**, is the
intensity of the scattered light as a function of the
5   growth time. During the initial nucleation period, an
increase in the scattered light is observed, which can
be related to mechanism of heteroepitaxial nucleation
and initial overgrowth, which evolves into the finally
observed surface roughness of the epitaxial layer.

10   The inserts **106**, **108** in Figure 2 show
sections of the amplitude modulated fine structure **110**
on top of the reflected radiation signal **46** which is
maintained throughout the entire layer growth. The
periodicity of this fine structure and its amplitude
15   modulation is strongly related to a complete cycle
sequence, which is built up by a TBP pulse of length
"a", followed by a delay "x", a TEG pulse of length "b"
and a second delay of the length "y". Best deposition
conditions are found for a pulse width ratio
20   $a:b=0.8:0.2$ with a flow rate ratio for TBP:TEG of
$0.5:0.06$ sccm, which results in a total dose ratio of
25:1 for TBP and TEG, respectively.

Figure 3A graphically illustrates a pulse
sequence for the TBP and TEG sources with a delay of 3
25   sec ($x:y=1.2sec:1.8sec$). During the entire deposition,
a constant flow of hydrogen is introduced. The growth
rate per cycle can be calculated from the overall
growth of the entire film and is estimated to be
3.18 ± 0.1 Å/cycle. Figure 3B graphically illustrates
30   the corresponding reflected intensity signal, and
illustrates the fine structure **110** of Figure 2.

Varying the total delay times between the
source pulses results in different growth times per
cycle sequence from 2Å/cycle to 3.6Å/cycle for 0.5 sec
35   to 6 sec delay, respectively. The observed amplitude
modulated fine structure changes according to the
change in the growth rate per cycle, shown as graphs

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(a)-(c) in Figure 4. Figure 4 shows the periodicity for 2 sec (a), 3 sec (b) and 6 sec delay (c) between the source pulses of the same precursor. Initial results indicate a close relationship of growth rate
5 per cycle and the length of the amplitude modulated fine structure, which may be correlated to a periodic reproduction of the original surface topography.

Accordingly, in the case of heteroepitaxy, an interference modulation 102 of the intensity of the
10 reflected radiation signal is observed, which contains information concerning the evolution of the optical properties as well as a record of the growth rate for the entire duration of layer deposition. Changes in the extrema (maxima 112, 114 and/or minima 122, 124) of
15 this signal provide information about deviations in bulk dielectric properties of the growing layer caused by absorption and inhomogeneities in the refractive index of the layer as well as changes in the surface roughness.

20   Furthermore, under the conditions of Pulsed Chemical Beam Epitaxy (PCBE), the reflected intensity contains a periodic oscillation 110 that is superimposed on the interference signal 102 with an Å scale period, and is maintained over thousands of Å of
25 film growth. The periodicity of this fine structure 110 matches the period of the sequence of precursor pulses of the PCBE process. Also, an amplitude modulation of the superimposed oscillation is observed which may be understood on the basis of the results of
30 Brewster's angle reflection spectroscopy studies of homoepitaxial growth. This amplitude modulation is best illustrated in Figure 4 described below.

Under the conditions of homoepitaxy, the interference oscillations 102 in the reflected
35 radiation signal cease to exist since the epitaxial layer and the substrate have the same dielectric function. However, the fine structure 110 can still be

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observed and may be utilized for analysis of the growth
mechanism. Moreover, in conjunction with the
observation of heteroepitaxial growth for the same
material, real-time monitoring of the growth rate may
5   be obtained.

In particular, growth of a first layer of a
first material on a first substrate of the first
material to form a homostructure is monitored by first
depositing a second layer of the first material on a
10 second substrate of a second material to form a
heterostructure. Polarized radiation is impinged on
the second layer during deposition thereof on the
second substrate at an angle which is approximately
equal to the Brewster's angle for the second substrate.
15 Radiation which is detected from the heterostructure
during the deposition is detected to produce an
interference signal 102 having a predetermined
periodicity. Then, the first layer is deposited on the
first substrate to form a homostructure. During this
20 deposition, polarized radiation is impinged on the
first layer during deposition thereof on the first
substrate at an angle which is approximately equal to
the Brewster's angle for the first substrate.
Radiation which is reflected from the homostructure is
25 detected to produce a fine signal 110 which has a
periodicity which is substantially higher than the
predetermined periodicity of the interference signal
102. The fine signal 110 is then calibrated using the
predetermined periodicity of the interference signal
30 102 and the calibrated fine signal is monitored during
the deposition to monitor growth of the first layer.

The intensity of the maxima 112, 114 in the
reflected radiation signal is determined by absorption
in the film and by scattering of the laser beam at its
35 surface. Accordingly, extrema in the interference
signal are detected and a ratio of selected extrema is
formulated. For example, a ratio of adjacent maxima is

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formulated. If this ratio deviates by more than a predetermined threshold value from unity, there may be an indication that the growth is proceeding unsatisfactorily, and the deposition process may be
5   terminated. Alternatively, the deviation signal may be used to change control parameters of the growth process to control the ratio to a predetermined value.

Since absorption also affects the residual reflectance at the position of the minima **122**, **124** in
10 the reflected radiation signal, which in the experiment depicted in Figure 2 does not change significantly, the reduction of the intensity between adjacent maxima **112**, **114** shown in Figure 2 is primarily caused by scattering. This is in accord with the observation of
15 increasing intensity of the associated scattered light (**104** in Figure 2) with increasing growth time/film thickness.

Accordingly, growth of a layer on a substrate in a chamber to form a structure is monitored by
20 pulsing at least one precursor of the layer in the chamber at a predetermined periodicity to deposit the layer on the substrate. Polarized radiation is impinged on the layer during deposition thereof on the substrate at an angle which is approximately equal to
25 the Brewster's angle for the substrate. Radiation which is reflected from the structure during deposition of the layer is detected to produce a first signal having the predetermined periodicity. Radiation which is scattered from the structure during deposition is
30 also detected to produce a second signal. The first and second signals are correlated to produce a third signal having a reduced scattering component relative to the first signal. This third signal is then monitored during deposition to monitor growth of the
35 layer. Note that at the onset of heteroepitaxial growth, a peak **116** is observed in the scattered light intensity trace, which provides information on the

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initial nucleation and overgrowth phase of the
heteroepitaxial process.

　　　　　Still referring to Figure 2, an amplitude-
modulated periodic fine structure on the reflected
5　intensity that is particularly pronounced on the rising
slope and maxima of the modulated interference signal
is maintained over the entire duration of layer growth.
The period of this fine structure and of its amplitude
modulation do not change between adjacent maxima at the
10　interference distance, as illustrated in the expanded
insets **106**, **108** in Figure 2. Each peak in the fine
structure corresponds to a specific cycle of the
precursor sequence that starts with a TBP pulse and is
followed by a pause of fixed duration, a TEG pulse and
15　a second pause of another fixed duration.

　　　　　Under the conditions of homoepitaxy, the
interference signal modulation vanishes because of the
absence of interference in the homoepitaxial film, but
the fine structure that is related to the changes in
20　the optical properties in the vicinity of the surface
is maintained. The fine structure of the interference
oscillations is also maintained under conditions of
heteroepitaxy. This effect may be modeled assuming a
very thin surface layer with a dielectric function that
25　differs from the underlying film, extending the model
to a multilayer stack. Figure 5 shows the reflected
radiation signal **46** and the scattered light signal **48**
for the initial stage of GaP homoepitaxy on a GaP (001)
substrate wafer. Both the reflected and the scattered
30　light signals show amplitude modulations that are
correlated, indicating that the amplitude in the fine
structure is related to cyclic changes in the surface
structure at a scale that is commensurate with the
scattering process. The amplitude modulation of the
35　amplitude modulated reflected radiation signal is
detected and compared to a reference to monitor growth
during deposition.

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Referring now to Figure 6, detection of the imaginary part of the dielectric function of the layer from the turning points in the fine structure is graphically illustrated. Figure 6 illustrates the time

5 evolution of the fine signal 110 during growth of a layer as a function of the imaginary part of the dielectric function ϵ_{P2} for real part of the dielectric function $\epsilon_{P1}=6.0$ of the layer. As shown, a well-pronounced amplitude modulated fine structure 110

10 superimposed on the interference oscillation 102, is observed in all cases, even without an assumed absorption in the surface reaction layer where $\epsilon_{P2}=0$. With increasing absorption in the surface reaction layer, the amplitude in the fine structure increases.

15 For $\epsilon_{P2}=0$ (the bottom curve in Figure 6), the minimum amplitude of the fine structure occurs at the minima and maxima of the interference oscillations. However, for increasing imaginary part of the dielectric constant ($\epsilon_{P2}=4$, 8 and 12), the minimum

20 amplitude of the amplitude modulated fine structure shifts away from the minimum of the interference signal. Figure 7 illustrates an enlargement of the fine structure of Figure 6 adjacent the minimum of the interference signal. The positions marked with an

25 arrow indicate the positions where the optical response to the first TBP pulse in the cycle sequence changes sign corresponding to minimum amplitude of the amplitude modulated fine structure. These turning points are shifted toward smaller times or smaller film

30 thicknesses with greater absorption, allowing a highly accurate measurement of the absorptivity of the layer. Accordingly, the location of the minimum of the fine signal relative to the minimum of the interference signal may be used to calculate the imaginary part of

35 the dielectric constant of the layer.

Referring now to Figures 8A-8D, measurements of rise and fall times relative to precursor cycle

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sequences are shown. Surface kinetic data can be
obtained by analyzing the rise and decay transients of
the fine structure. Figures 8A-8D show the temporal
evolution of the surface layer, the increase in bulk
5   (GaP) film thickness and the related changes in the
reflectivity during several cycle sequences. The
precursor cycle sequence, shown in Figure 8A, includes
a TBP pulse of length "a"=0.8 sec, followed by a delay
"x" of 0.6 sec, a TEG pulse of length "b"=0.3 sec and a
10   second delay "y"=1.3 sec.

Figure 8B shows calculated changes in the
thickness of the surface layer for maximal surface
coverage d_{cov}=3Å and a complex dielectric function for
the surface layer of ϵ_{p2}=(8.0, 2.0). The exponential
15   increase of the surface layer is set to a_{TBP}=1.0 and the
decay factor α_{TEG} describing the decrease of the surface
layer is set to 2.0. The time dependent increase of
the bulk film thickness during the cycle sequence is
shown in Figure 8C for a growth rate of 3Å per cycle.
20   Figure 8D shows the calculated changes in the
reflectivity during the time evolution of the surface
layer and the bulk film growth process with λ=6328Å,
angle of incidence φ=72°, a complex dielectric function
for the silicon substrate ϵ_{si}=(15.25, 0.17), a complex
25   dielectric function for the gallium phosphide bulk film
of ϵ_{GaP}=(11.11, 0.0). By analyzing the rise time **802**
and the fall time **804** of the fine signal, the "time
constants" of the layer forming system may be
determined to thereby obtain valuable information
30   concerning the surface kinetics of the system.

Accordingly, the evolution of the bulk
properties and growth rate are monitored using the
periodic structure in the reflectance based on
interference in the layer and on the residual minimum
35   reflectance due to both absorption and shifts in the
Brewster's angle position that are associated with the
changes in the imaginary and real parts of the

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dielectric function upon heteroepitaxial film growth. The evolution of the surface properties is monitored by the periodic fine structure in the intensity of the P-polarized reflected light, which is correlated with the switching cycles of the metal-organic precursor pulses and is amplitude-modulated in accord with the repeat cycle of the heteroepitaxial growth process.

In the drawings and specification, there have been disclosed typical preferred embodiments of the invention and, although specific terms are employed, they are used in a generic and descriptive sense only and not for purposes of limitation, the scope of the invention being set forth in the following claims.

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CLAIMS:

1. A method of monitoring formation of a layer on or in a substrate to form a heterostructure, comprising the steps of:

5   impinging polarized radiation on said layer during formation thereof on or in said substrate, at an angle which is approximately the Brewster's angle for said substrate;

     detecting radiation which is reflected from said heterostructure during said formation of said 10   layer to produce an interference signal having a predetermined periodicity;

     detecting extrema in said interference signal; and

     monitoring a ratio of selected extrema to 15   monitor formation of said layer.

2. A method according to Claim 1 wherein said monitoring step is followed by the step of controlling said formation of said layer on or in said substrate based upon said ratio of extrema.

20   3. A method according to Claim 2 wherein said controlling step comprises the steps of:

     comparing the ratio of extrema to a reference; and

     controlling said layer formation based upon 25   differences between the ratio of extrema and the reference.

4. A method of monitoring formation of a layer on or in a substrate to form a heterostructure, comprising the steps of:

30   impinging polarized radiation on said layer during formation thereof on or in said substrate, at an angle which is approximately the Brewster's angle for said substrate;

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detecting radiation which is reflected from said heterostructure during said formation of said layer to produce an interference signal having a predetermined periodicity; and

5   detecting a fine signal which is superimposed on said interference signal and which has periodicity substantially higher than said predetermined periodicity, to thereby monitor formation of said layer on or in a substrate.

10   5.   A method according to Claim 4 wherein said fine signal detecting step comprises the step of detecting the rise time and fall time of the fine signal to thereby monitor the kinetics of the formation of said layer on or in said substrate.

15   6.   A method according to Claim 4 further comprising the steps of:
       monitoring the location of minima in said interference signal;
       monitoring the location of amplitude
20 modulation minima in the amplitude modulated fine signal; and
       determining the imaginary part of the dielectric constant of the layer based upon the location of the amplitude modulation minima relative to
25 the interference signal minima.

7.   A method according to Claim 4 wherein said fine signal detecting step is followed by the step of controlling said formation of said layer on said substrate based upon said fine signal.

30   8.   A method according to Claim 7 wherein said controlling step comprises the steps of:
       comparing the monitored fine signal to a reference; and

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controlling said formation based upon differences between the compared fine signal and the reference.

9.   A method of monitoring formation of a
5   layer on or in a substrate in a chamber to form a structure, comprising the steps of:
pulsing at least one material in said chamber at a predetermined periodicity to form said layer on or in said substrate;
10   impinging polarized radiation on said layer during formation thereof on or in said substrate, at an angle which is approximately the Brewster's angle for said substrate or said layer;
detecting radiation which is reflected from
15   said structure during said formation of said layer to produce an amplitude modulated signal having said predetermined periodicity; and
monitoring the amplitude modulation of said amplitude modulated signal during said layer formation.

20   10.   A method according to Claim 9 wherein said layer is different from said substrate to produce a heterostructure, and wherein said detecting step comprises the step of detecting radiation which is reflected from said heterostructure during said
25   formation of said layer to produce an interference signal having a second periodicity and including said amplitude modulated signal superimposed thereon, wherein said predetermined periodicity is substantially greater than said second periodicity.

30   11.   A method according to Claim 10 wherein said monitoring step further comprises the steps of:
detecting extrema in said interference signal; and
monitoring a ratio of selected extrema.

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12. A method according to Claim 9 wherein said monitoring step is followed by the step of controlling said formation of said layer on said substrate based upon said monitored amplitude modulation of said amplitude modulated signal.

13. A method according to Claim 12 wherein said controlling step comprises the steps of:

comparing the monitored amplitude modulated signal to a reference; and

controlling said layer formation based upon differences between the compared amplitude modulated signal and the reference.

14. A method of monitoring formation of a first layer of a first material on or in a first substrate of said first material to form a homostructure, comprising the steps of:

forming a second layer of said first material on a second substrate of a second material to form a heterostructure;

impinging polarized radiation on said second layer during formation thereof on said second substrate, at an angle which is approximately the Brewster's angle for said second substrate;

detecting radiation which is reflected from said heterostructure during said layer formation to produce an interference signal having a predetermined periodicity;

forming said first layer on said first substrate to form a homostructure;

impinging polarized radiation on said first layer during formation thereof on said first substrate, at an angle which is approximately equal to the Brewster's angle for said first substrate;

detecting radiation which is reflected from said homostructure during said layer formation to

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produce a fine signal which has a periodicity which is substantially higher than said predetermined periodicity;

calibrating said fine signal using said
5   predetermined periodicity of said interference signal; and

monitoring the calibrated fine signal during said layer formation.

15.   A method according to Claim 14 wherein
10   said monitoring step is followed by the step of controlling said formation of said first layer on said first substrate based upon said monitored calibrated fine signal.

16.   A method according to Claim 15 wherein
15   said controlling step comprises the steps of:

comparing the monitored calibrated fine signal to a reference; and

controlling said layer formation based upon differences between the compared calibrated fine signal
20   and the reference.

17.   A method of monitoring formation of a layer on or in a substrate in a chamber to form a structure, comprising the steps of:

pulsing at least one material in said chamber
25   at a predetermined periodicity to form said layer on or in said substrate;

impinging polarized radiation on said layer during formation thereof on or in said substrate, at an angle which is approximately the Brewster's angle for
30   said substrate;

detecting radiation which is reflected from said structure during said formation of said layer to produce a first signal having said predetermined periodicity;

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detecting radiation which is scattered from said structure during formation of said layer to produce a second signal;

5   correlating said first and second signals to produce a third signal; and

   monitoring said third signal during said deposition to monitor formation of said layer.

18. A method according to Claim 17 wherein said correlating step comprises the step of subtracting

10 said second signal from said first signal to produce said third signal having reduced scattering component relative to said first signal.

19. A method according to Claim 17 wherein said layer is different from said substrate to produce

15 a heterostructure, and wherein said reflected radiation detecting step comprises the step of detecting radiation which is reflected from said heterostructure during said formation of said layer to produce an interference signal having a second periodicity and

20 including said first signal superimposed thereon, wherein said predetermined periodicity is substantially greater than said second periodicity.

20. A method according to Claim 17 wherein said monitoring step comprises the steps of:

25   detecting extrema in said third signal; and

   monitoring a ratio of selected extrema to monitor formation of said layer.

21. A method according to Claim 17 wherein said monitoring step is followed by the step of

30 controlling said formation of said layer on said substrate based upon said monitored third signal.

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22. A method according to Claim 21 wherein said controlling step comprises the steps of:

comparing the monitored third signal to a reference; and

5   controlling said layer formation based upon differences between the compared third signal and the reference.

23. A system for monitoring formation of a layer on or in a substrate to form a heterostructure,

10   comprising:

means for impinging polarized radiation on said layer during formation thereof on or in said substrate, at an angle which is approximately the Brewster's angle for said substrate;

15   means for detecting radiation which is reflected from said heterostructure during said formation of said layer to produce an interference signal having a predetermined periodicity;

means for detecting extrema in said

20   interference signal; and

means for monitoring a ratio of selected extrema to monitor formation of said layer.

24. A system according to Claim 23 wherein said monitoring means further comprises means for

25   detecting a fine signal which is superimposed on said interference signal and which has periodicity substantially higher than said predetermined periodicity.

25. A system according to Claim 23 further

30   comprising means, responsive to said monitoring means, for controlling said formation of said layer on said substrate.

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26. A system according to Claim 25 wherein said controlling means comprises:

means for comparing the ratio of extrema to a reference; and

5   means, responsive to said comparing means, for controlling said layer formation based upon differences between the ratio of extrema and the reference.

27. A system for monitoring formation of a
10 layer on or in a substrate in a chamber to form a structure, comprising:

means for pulsing at least one material in said chamber at a predetermined periodicity to form said layer on said substrate;

15   means for impinging polarized radiation on said layer during formation thereof on or in said substrate, at an angle which is approximately the Brewster's angle for said substrate;

means for detecting radiation which is
20 reflected from said structure during said formation of said layer to produce an amplitude modulated signal having said predetermined periodicity; and

means, responsive to said detecting means, for monitoring the amplitude modulation of said
25 amplitude modulated signal during said layer formation.

28. A system according to Claim 27 wherein said layer is different from said substrate to produce a heterostructure, and wherein said detecting means comprises means for detecting radiation which is
30 reflected from said heterostructure during said formation of said layer to produce an interference signal having a second periodicity and including said amplitude modulated signal superimposed thereon, wherein said predetermined periodicity is substantially
35 greater than said second periodicity.

29. A system according to Claim 28 wherein
said monitoring means further comprises means for
monitoring the second periodicity of said interference
signal.

5   30. A system according to Claim 28 wherein
said monitoring means further comprises:
             means for detecting extrema in said
interference signal; and
             means for monitoring a ratio of selected
10 extrema.

             31. A system according to Claim 27 further
comprising means, responsive to said monitoring means,
for controlling said formation of said layer on or in
said substrate.

15   32. A system according to Claim 31 wherein
said controlling means comprises:
             means for comparing the amplitude modulated
signal to a reference; and
             means, responsive to said comparing means,
20 for controlling said layer formation based upon
differences between the amplitude modulated signal and
the reference.

             33. A system for monitoring formation of a
layer on or in a substrate in a chamber to form a
25 structure, comprising the steps of:
             means for pulsing at least one material in
said chamber at a predetermined periodicity to form
said layer on said substrate;
             means for impinging polarized radiation on
30 said layer during formation thereof on said substrate,
at an angle which is approximately the Brewster's angle
for said substrate;

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first means for detecting radiation which is reflected from said structure during said formation of said layer to produce a first signal having said predetermined periodicity;

5   second means for detecting radiation which is scattered from said structure during formation of said layer to produce a second signal;

means, responsive to said first and second detecting means, for correlating said first and second

10   signals to produce a third signal; and

means, responsive to said correlating means, for monitoring said third signal during said formation to monitor formation of said layer.

34.   A system according to Claim 33 wherein

15   said correlating means comprises means for subtracting said second signal from said first signal to produce said third signal having reduced scattering component relative to said first signal.

35.   A system according to Claim 33 further

20   comprising means, responsive to said monitoring means, for controlling said formation of said layer on said substrate based upon said third signal.

36.   A system according to Claim 35 wherein said controlling means comprises:

25   means for comparing the third signal to a reference; and

means, responsive to said comparing means, for controlling said formation based upon differences between the compared third signal and the reference.
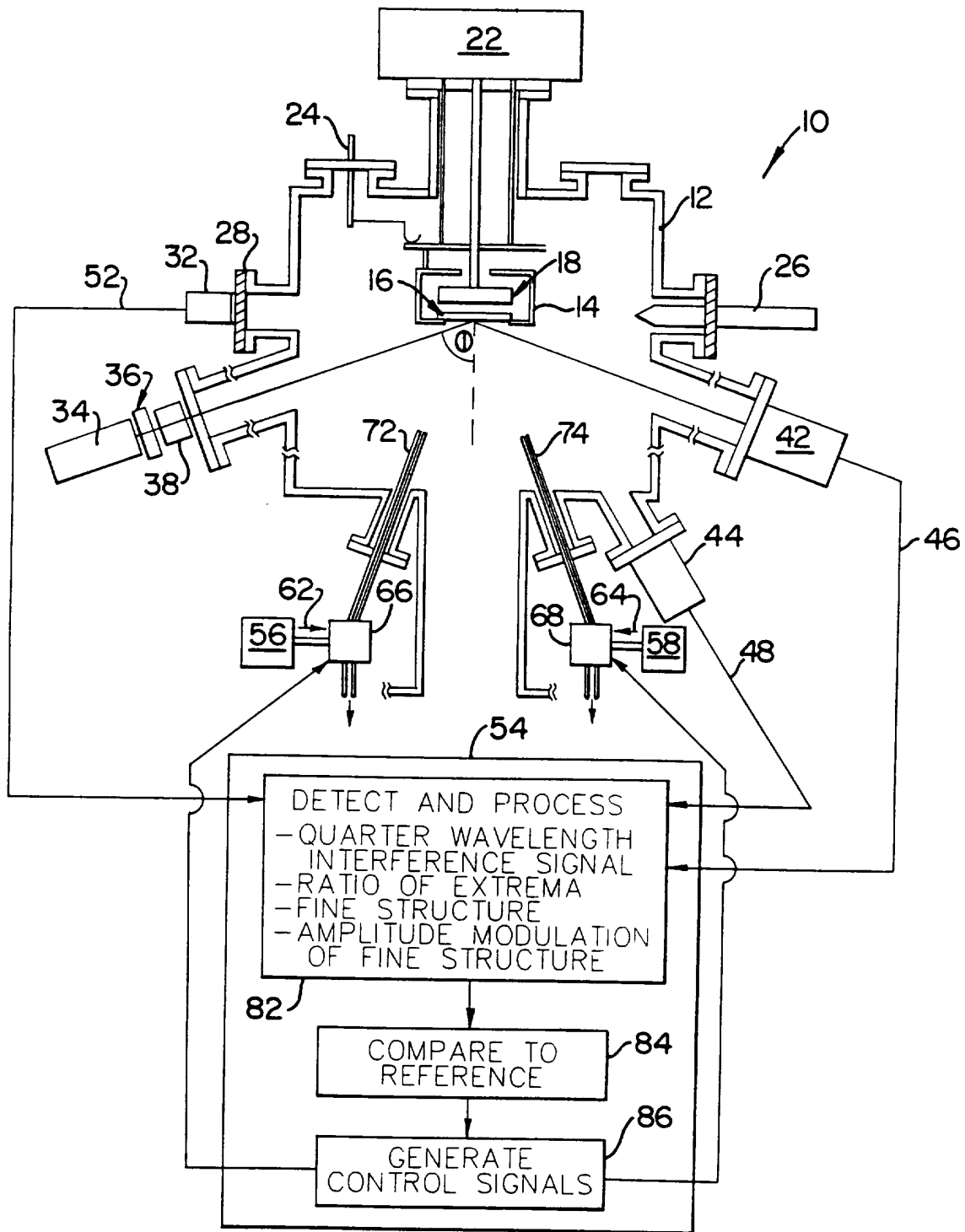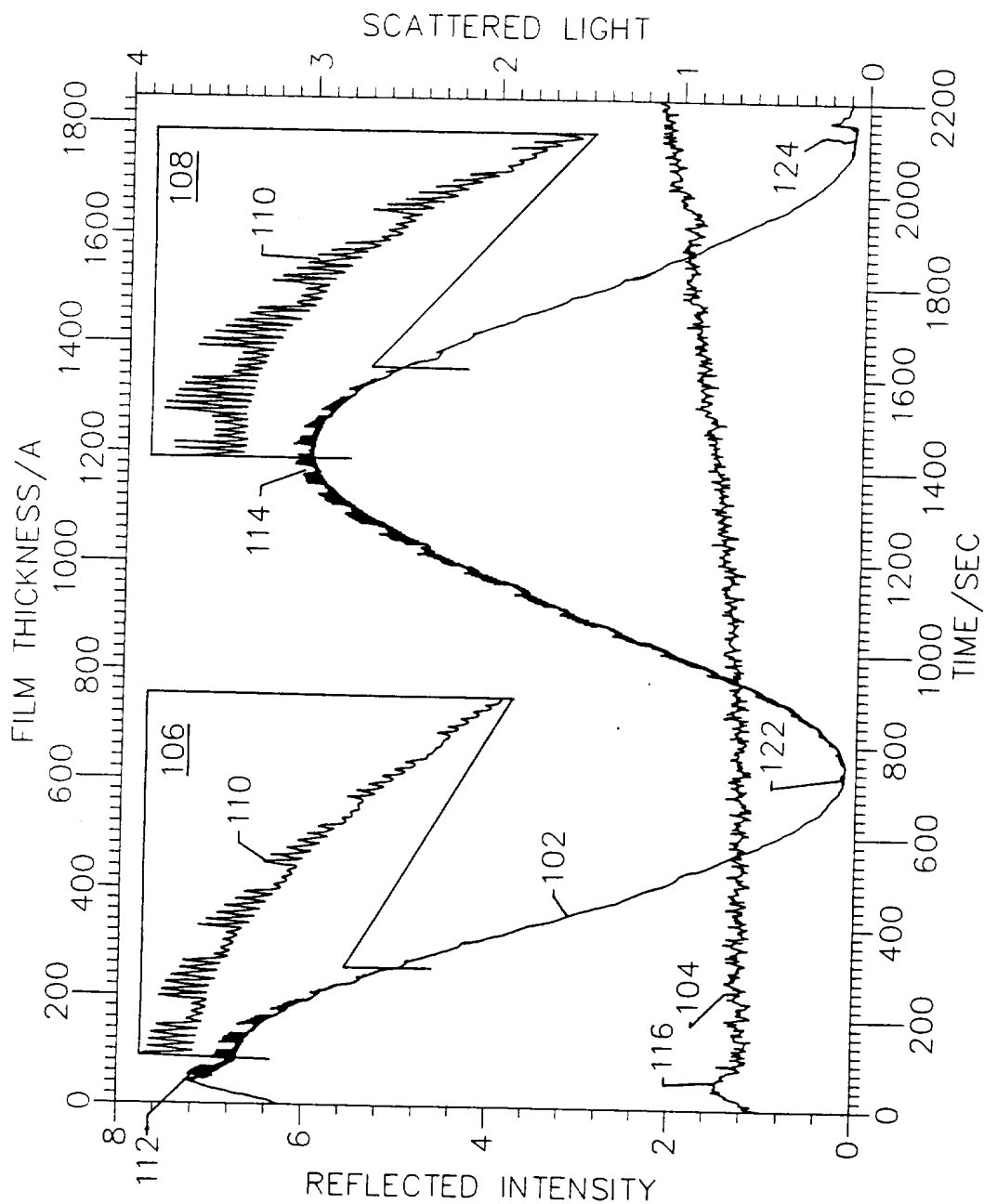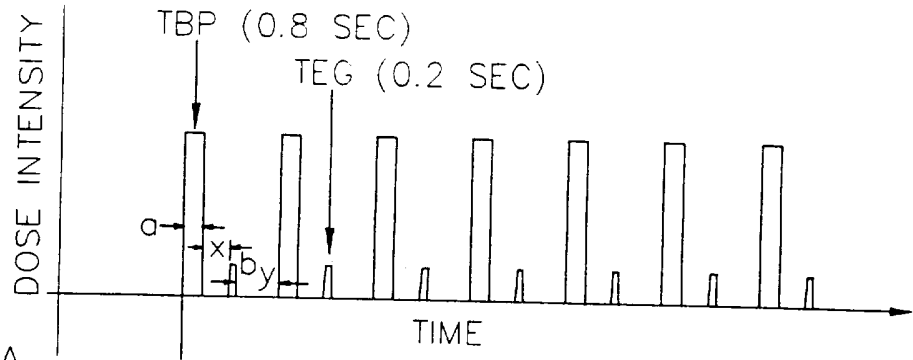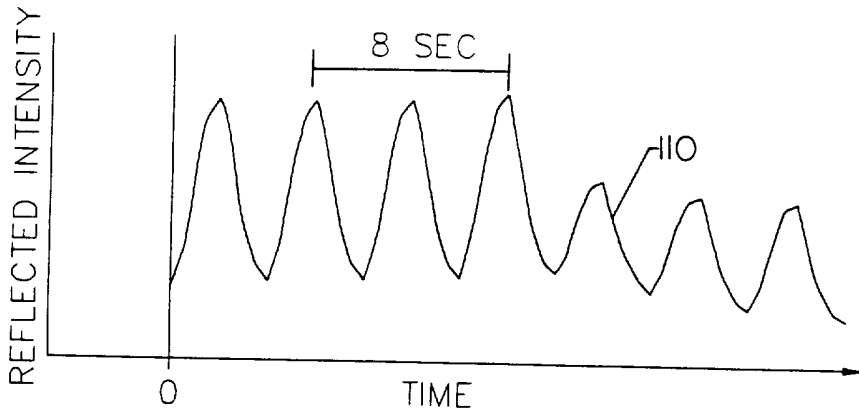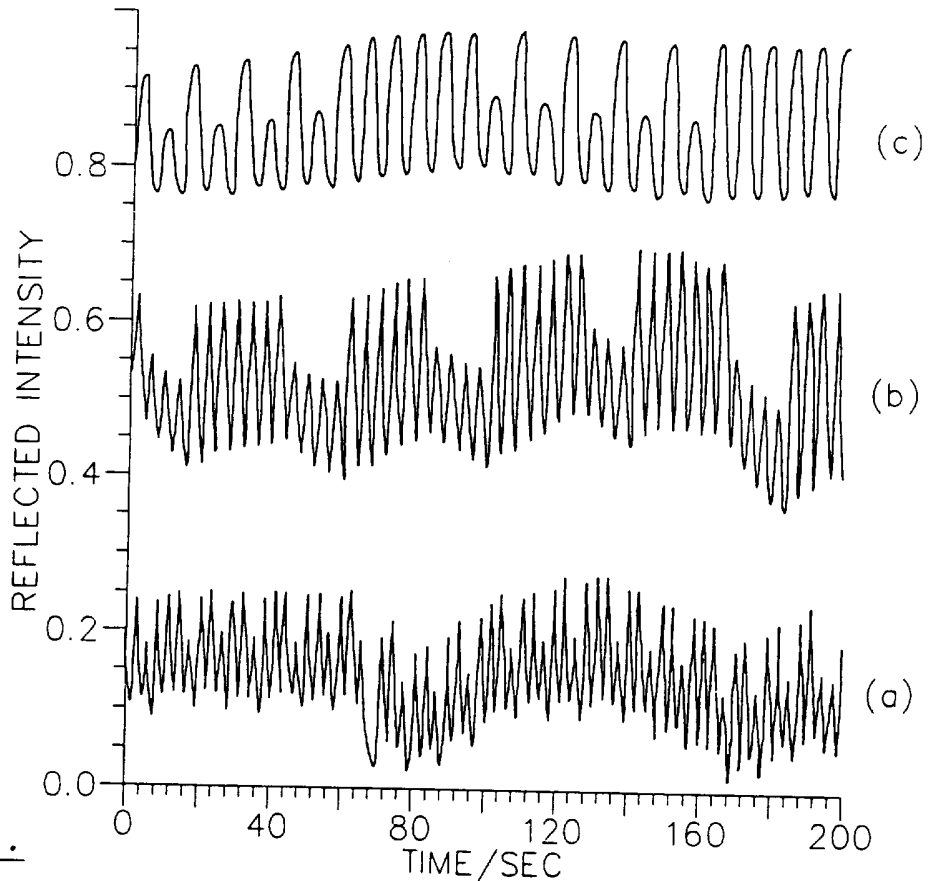
FIG. 1.

FIG. 2.
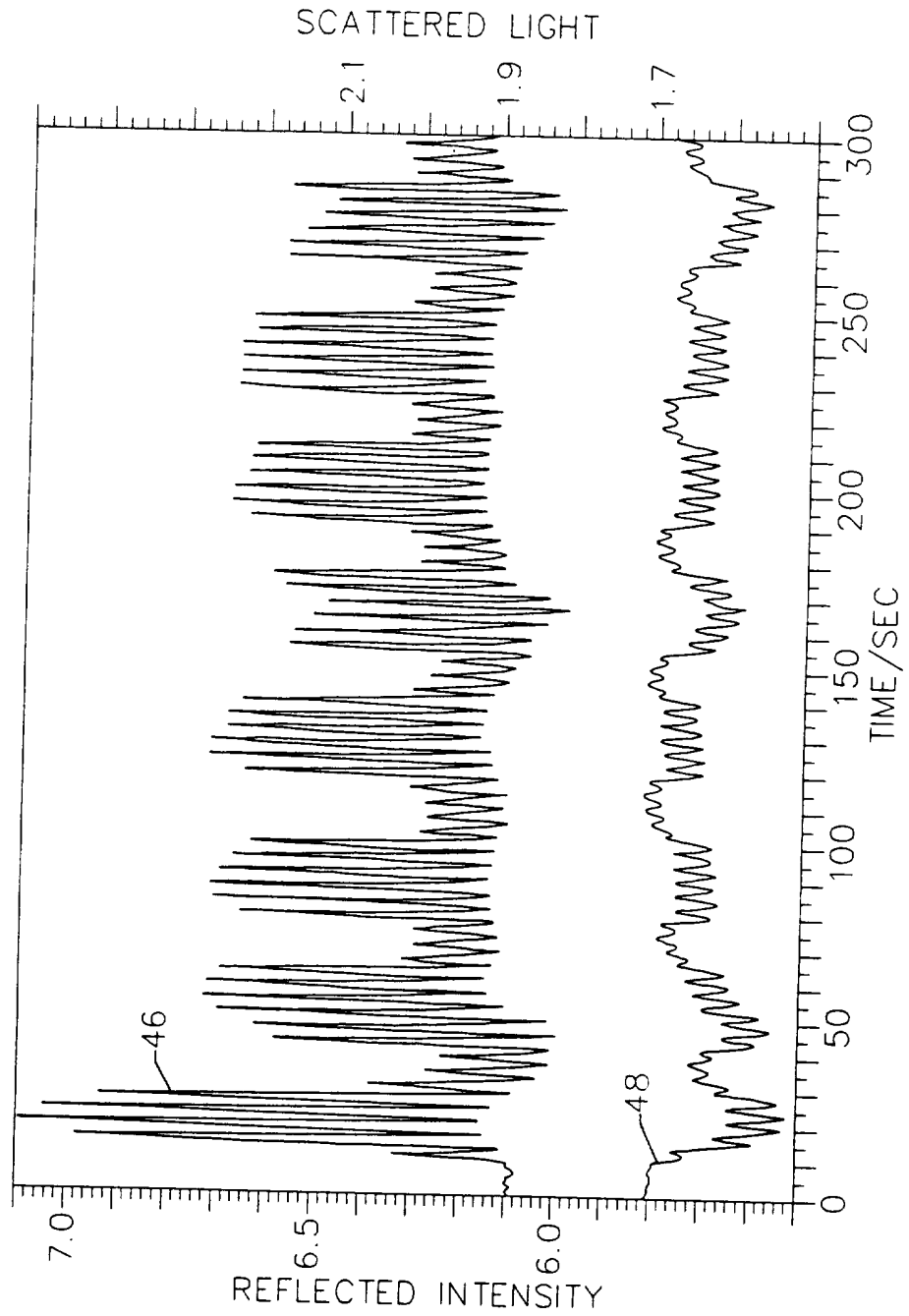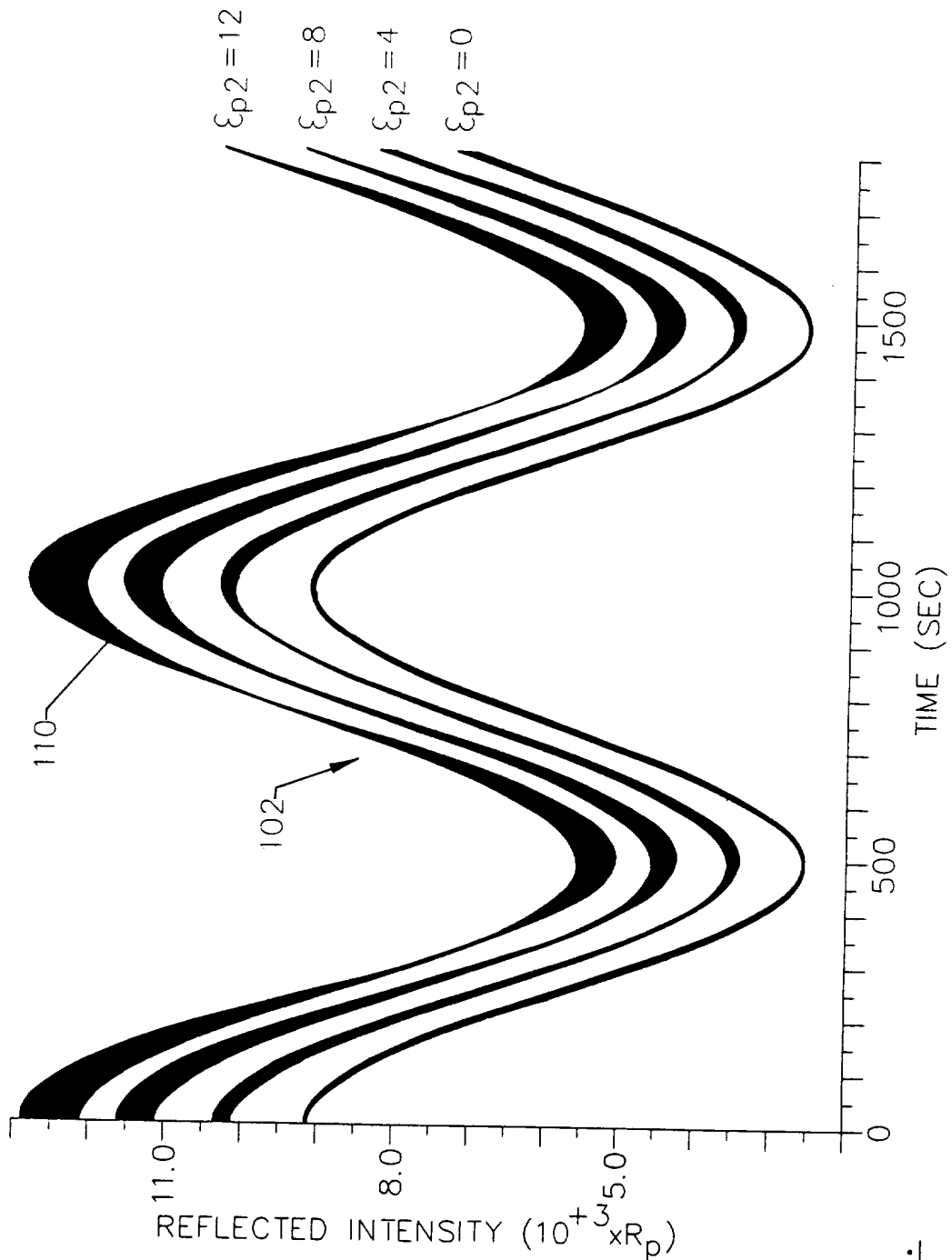
FIG. 3A.

FIG. 3B.

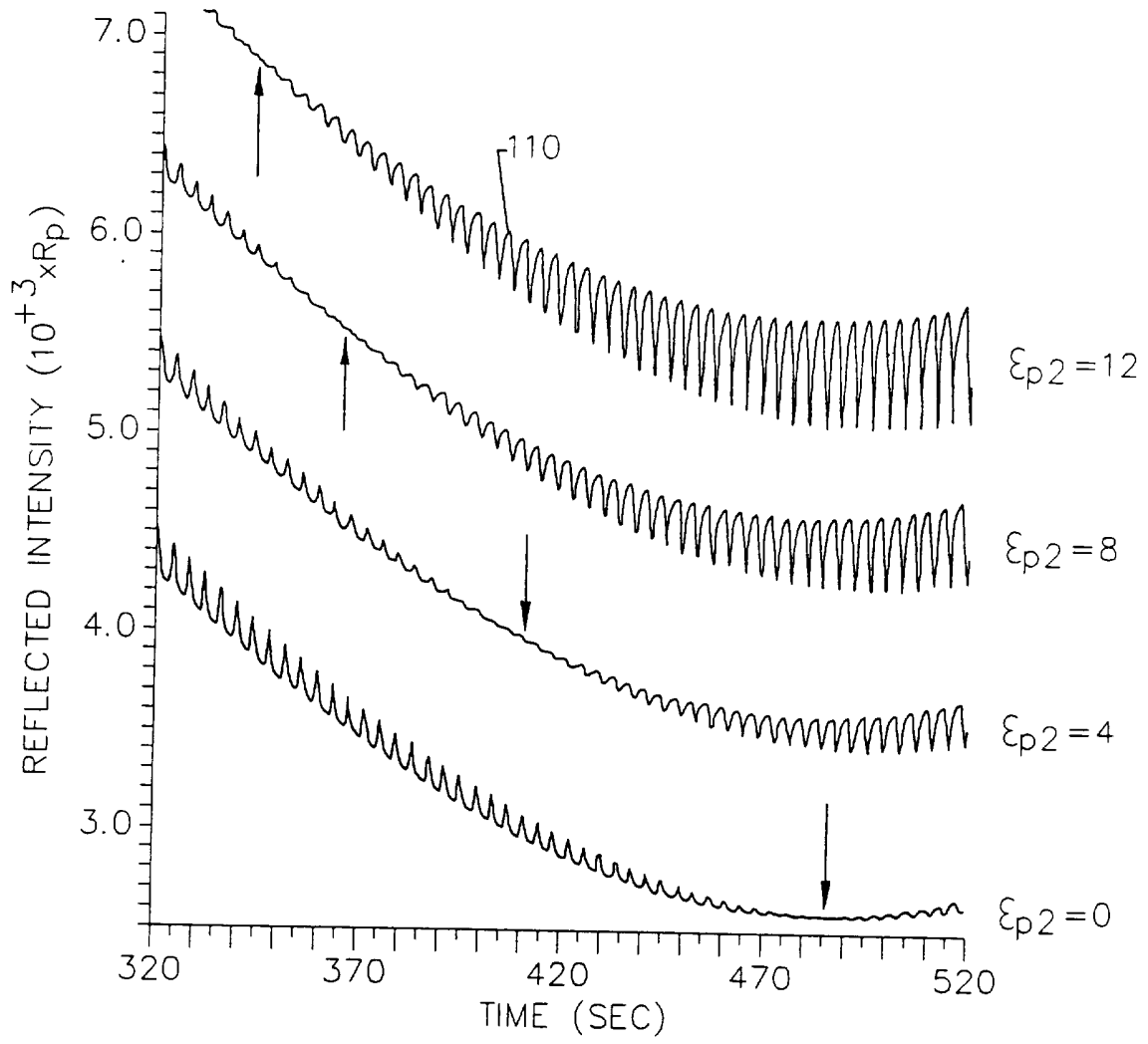FIG. 4.

SCATTERED LIGHT

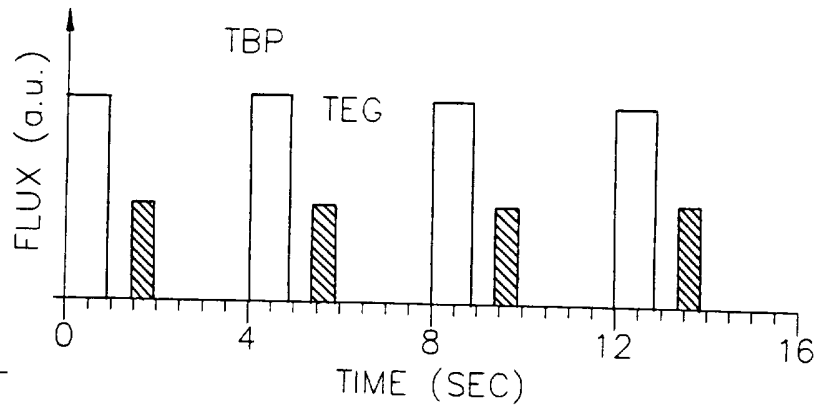REFLECTED INTENSITY

TIME/SEC

FIG. 5.

FIG. 6.

FIG. 7.

FIG. 8A.

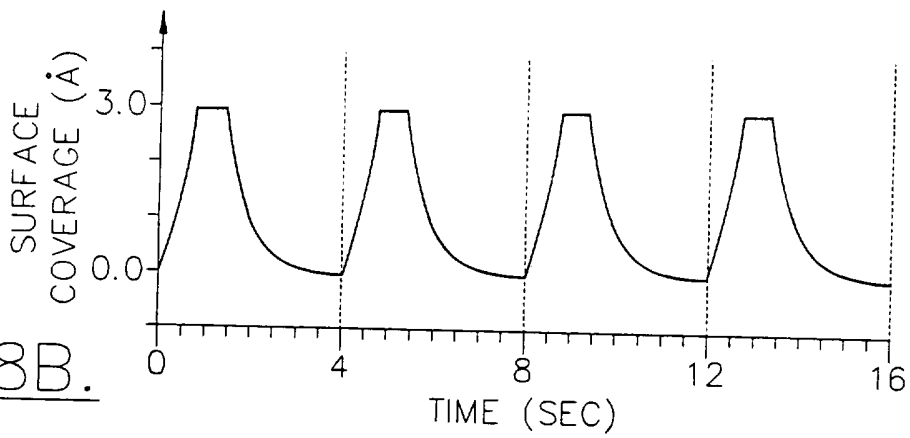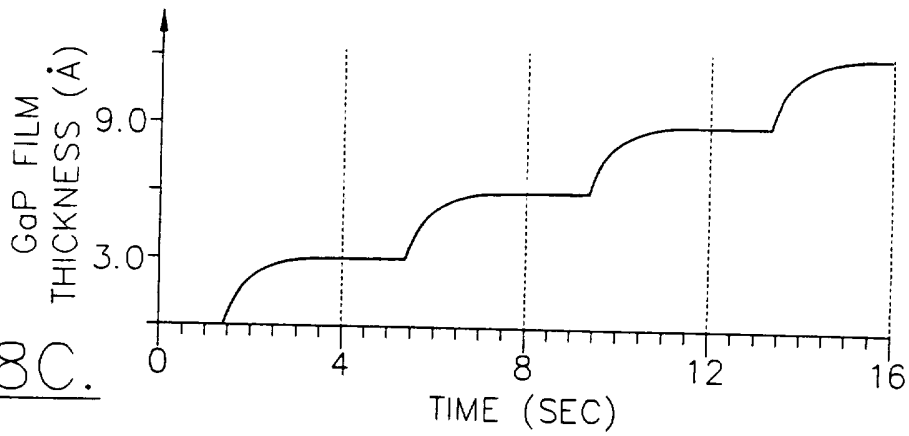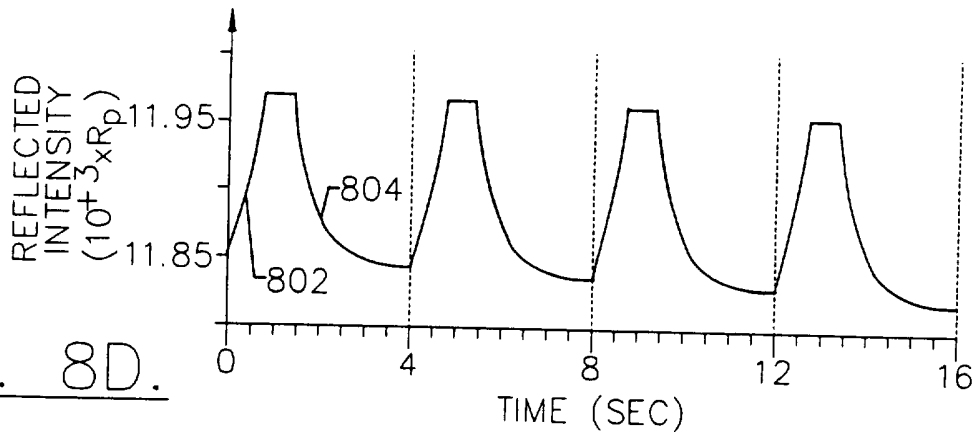FIG. 8B.

FIG. 8C.

FIG. 8D.

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC(6)   :H01L 21/66; B05D 1/00
US CL   : 437/8; 156/626; 472/9, 10; 117/85, 86; 118/688; 156/345
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
Minimum documentation searched (classification system followed by classification symbols)
U.S. :   437/8; 156/626; 472/9, 10; 117/85, 86; 118/688; 156/345 29/D16

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
JPO, CA, USPAT: Brewster' angle absorption; reflectance; SPt; surface photo absorption; polarization; Brewster; spectroscopy, ellipsometry, birds

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y --- Y	DIETZ, et al., "AN OPTICAL IN-SITU METHOD FOR LAYER GROWTH CHARACTERIZATION", APPLIED SURFACE SCIENCE, Vol. 69, 1993 pp 350-354 (see abstract; pg 351, Col. 2)	1, 23 ---------- 2, 3
X ---- Y	HORIKOSHI, et al., "OPTICAL INVESTIGATION OF GaAs GROWTH PROCESS IN MOLECULAR BEAM EPITAXY AND MIGRATION-ENHANCED EPITAXY" JOURNAL OF CRYSTAL GROWTH, VOL. 111, 1991, pp. 200-204 (see Abstract; Fig 5)	9, 23-25, 27-31 ---------------- 4, 5, 7, 8, 10-13, 26, 32
X ---- Y	DIETZ, et al., "IN-SITU MULTILAYER FILM GROWTH CHARCTERIZATION BY BREWSTER ANGLE REFLECTANCE DIFFERENTIAL SPECTROSCOPY", MAT. RES. SOC. SYMP. PROC. , VOL. 324, 1994, pp 27-32	1, 23 --------- 2, 3

[X]	Further documents are listed in the continuation of Box C.	[ ]	See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance		
"E"	earlier document published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed	"&"	document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
18 NOVEMBER 1995	04 JAN 1996

Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	Authorized officer BRUCE BRENEMAN
Facsimile No. (703) 305-3230	Telephone No. (703) 308-3324

Form PCT/ISA/210 (second sheet)(July 1992)*

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	KOBAYASHI, ET AL., "IN-SITU MONTORING AND CONTROL OF ATOMIC LAYER EPITAXY BY SURFACE PHOTO ABSORPTION", THIN SOLID FILMS, VOL. 225, 1993, pp 32-39	
X --- Y	US,A, 5,091,320 (ASPNES ET AL.) 25 FEBRUARY 1992, ABSTRACT, COL. 6, LINES 20-24, SUMMARY, COLUMN 5, LINES 35-54, COLUMN 8, LINES 5-12, COLUMNS 10-14	1, 23 ---------------- 2-3, 25, 26