OPTICAL DIAGNOSTICS FOR THIN FILM PROCESSING

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Abstract  Optical diagnostics are used to probe the plasma or neutral gas above the substrate, particles in the gas or on the surface, the film surface and reactor walls, the film itself, and the substrate during thin film processing. The development and application of optical probes are highlighted, in particular for analyzing plasma/gas phase intermediates and products and film composition, and performing metrology, thermometry, and endpoint detection and control. Probing etching (particularly plasma etching) and deposition (particularly epitaxy) are emphasized.

INTRODUCTION

Optical spectroscopy and other optical probes are widely used to monitor thin film processes, such as etching and deposition, by examining the gas or plasma above the substrate, the thin film and its surface, and the substrate in situ and often in real time during the process. This probing is done to understand the fundamental chemical steps of the process, optimize process parameters, and control manufacturing. This article highlights the literature in this field since the publication of the book Optical Diagnostics for Thin Film Processing by the author in 1996 (1). The development of new probes and the use of established probes in novel systems are emphasized. For details about established diagnostics themselves and earlier references, the reader is invited to refer to (1).

Optical probes are often nonintrusive and can usually probe film processes through a gas ambient, enabling real-time in situ analysis. Measuring the types, densities, and state distributions of atoms, radicals, molecules, particles, and, in plasmas, electrons and ions, are common goals in analyzing species in the gas or plasma atop the wafer during processing. Measuring film composition, thickness, uniformity, and roughness are potential goals in analyzing the film being deposited or etched (2). Thermometry (1, 3), monitoring the composition of the film surface, metrology (film thickness and lateral dimensions/topography of patterned films), and endpoint detection are four common goals of in situ diagnostics.
automatic control of film processing are addressed only briefly below; they are detailed in References 1 and 4.

In this context, “optical” usually denotes from the mid-UV to the mid-IR. In many instances different optical probes are used together, such as those probing above the substrate with those of the surface and film, and with nonoptical probes. Extensive modeling and theory are sometimes needed, as in modeling film composition with multilayer models in spectroscopic ellipsometry (SE); ab initio calculation of surface structure and the optical response of surfaces for infrared probing and reflectance difference spectroscopy (RDS); and rapid numerical analysis schemes for real-time control.

Optical probes are routinely applied to the most common modes of etching and deposition (5). The most common types of plasma etching use inductively coupled plasma (ICP), reactive ion etching (RIE), and electron cyclotron resonance (ECR) plasma reactors. Common modes of deposition are chemical vapor deposition (CVD)—including metallo-organic CVD (MOCVD) [also called metallo-organic vapor phase epitaxy (MOVPE)] and plasma enhanced (or assisted) CVD (PECVD or PACVD)—and sputtering—including magnetron sputtering, molecular beam epitaxy (MBE), various MBE/MOCVD hybrids, pulsed laser deposition (PLD), and thermal and electron-beam evaporation.

PLASMA AND NEUTRAL GAS PHASES

Studies of processing plasmas are concerned with determining the types of neutrals and ionic species, their densities, and the electron-energy distribution functions (EEDFs), which can sometimes be characterized by an electron temperature $T_e$. The most successful mechanistic studies of plasma processing combine this knowledge of the composition of the plasma with the composition of the surface during processing and the etch/deposition rate. Optical probing is now also being used to study the residues on the walls of plasma (and other) reactors that build up during use. These residues can affect recombination kinetics, which change plasma properties and therefore process (etch) rates, and can flake off to become an important source of particulate contamination, which can lead to defects in lithographic patterning. Quantifying source fluxes is important in physical deposition processes, such as MBE.

Optical Emission Spectroscopy

Optical emission spectroscopy (OES) is a convenient tool for semiquantitative analysis of processing plasmas and is widely used to assess trends in plasma etching (6) and deposition, including sputter deposition, and for process control (7). It provides information about the densities of a given excited state being probed and becomes a powerful quantitative tool of ground state density (which usually $\approx$ total density) when emission intensities of species of interest are compared to those from a stable rare gas reference, as in actinometry.
Studies of the etching by chlorine-containing plasmas have recently been extended beyond semiconductors and their oxides to other materials, such as high-K dielectrics, as in the monitoring of Cl, B, and BCI excited-state population during ICP etching of (Ba,Sr)TiO$_3$ by BCl$_3$/Cl$_2$/Ar mixtures (8). OES is now used during plasma modification or “treatment” of polymer surfaces, because this treatment sometimes involves a bit of etching or decomposing of the film, as in CN and CH identification during the oxygen plasma treatment of polyacrylonitrile (PAN) (9). OES is still widely used in deposition because it is simple and nonintrusive. For example, OES is often used to help optimize film performance during PECVD even though connections to the microscopic reaction steps are not always clear. For example, the ratio of OES intensity from C$_2$ and O during the PEVCD of zirconium oxide has been used to control the carbon incorporation in the films (10). Time-resolved OES helped probe the instability and target poisoning in the reactive sputtering process involving one metallic target (Ti) and two reactive gases (N$_2$ and O$_2$) in depositing oxynitride (11). OES, very widely used in PLD, can provide kinetic information, as from the interaction of the Cu laser ablation plume and a timed pulsed N$_2$O jet gas pulse to understand the growth of CuO (12).

OES has also been important in investigating more fundamental aspects of discharges used for processing films. “Inductively-coupled plasmas” can operate in an E ( capacitively coupled, dim) mode at lower rf powers and an H (inductively coupled, bright) mode at higher rf powers. At the sudden E-H mode transition, the ion and electron densities increase by an order of magnitude. OES has been used to quantitatively analyze E to H and H to E mode hysteresis in Ar/H$_2$, N$_2$/Ar, and N$_2$/H$_2$ ICPs (13).

Rotational, vibrational, and electronic “temperatures” in plasma reactors are now routinely made using well-established OES methods. In one example, the gas temperature in ICPs was measured by adding a trace amount of N$_2$ (2%–5%) and to determine the rotational temperature of the C$^3\Pi_u$ state from the ultraviolet C$^3\Pi_u \rightarrow$ B$^3\Pi_g$ emission (14); this presumes equilibration of the translational and rotational temperatures. The temperature increased with pressure and rf power, and was as high as 1250 K in 20 mTorr pressures (900 W, 0.36 W/cm$^2$), with most of this heating caused by the energy release in the dissociation of Cl$_2$.

One new and important application of OES is the evaluation of electron energy distribution functions (EEDFs). In the method of trace rare gas optical emission spectroscopy (TRG-OES), small amounts of He, Ne, Ar, Kr, and Xe (~1% each) are added to the plasma, and the intensities of many of the observed emission lines are compared with expectations of a kinetics model that includes known excitation cross sections and excitations from both the ground state and metastable states. Use of many lines (typically ~20 lines) in this analysis lessens some uncertainties (such as in the analysis of the contributions of metastables). TRG-OES was developed and applied to determine the EEDFs for several chlorine plasmas (15–18).

This method is most sensitive for energies just above the threshold excitation energies of the chosen actinometers. For Maxwellian distributions, the EEDF is described by an electron temperature $T_e$. For non-Maxwellian EEDFs, the
high-energy tail of the EEDF can be described by a $T_e$. In one example, $T_e$ in Cl$_2$/BCl$_3$/N$_2$ ICP etching plasmas was seen to decrease from to 2.3 eV to 1.4 eV as total pressure was increased from 3 mTorr to 40 mTorr (19); this trend of increasing $T_e$ with decreasing pressure is expected from the global model of plasmas (20). In Cl$_2$/Ar ICPs, $T_e$ was determined using only Kr and Xe emission lines (and not Ar lines) because of evidence of radiation trapping of the Ar lines (21). $T_e$ increased from $\sim$4.0 eV to $\sim$6.0 eV from predominantly Cl$_2$ to Ar inductive-mode plasmas (18 mTorr).

**OES ACTINOMETRY** In optical emission spectroscopy actinometry, the emission intensity at wavelength $\lambda_A$ from a species of interest $I(A^*, \lambda_A)$ from $A^*$, with ground state density $n_A$, is compared to that from a stable rare gas reference, the actinometer, $I(X, \lambda_X)$ from $X^*$, with ground state density $n_X$. Then, $n_A$ is obtained from

$$I(A, \lambda_A)/I(X, \lambda_X) = R_{A,X} n_A/n_X,$$

where $R_{A,X}$ is the ratio of the rate constants for exciting A and X.

The rare gas actinometer is chosen so the excitation energies of the emitting species of interest match as nearly as possible, to best overlap the match cross section versus electron energy. The emitting actinometer states should be chosen to minimize corrections due to emission from metastable stables. Corrections for changes in gas density (caused by changing gas temperature) and $T_e$ with rf power must also be included. There has been definitive progress recently on how to include these features, so that actinometric analysis can be more accurate.

OES actinometry is not a reliable indicator of ground-state species density when there is substantial (and unaccounted for) production of emitting species from dissociative excitation of stable species in the discharge (22), as was seen to be true for F, H, and O atoms in CHF$_3$/Ar/O$_2$ RIE plasmas and O atoms in several sources (23, 24). Including the effect of electron impact dissociation and dissociative attachment can improve the actinometric determination of Cl also (25), and is usually (and should be) included in the analysis.

Optical emission actinometry has been used in several investigations to determine Cl$_2$ and Cl densities in chlorine plasmas by comparing emission from Cl$_2$ (306.0 nm) or Cl emission (822.2 nm) to that from Xe (828.0 nm) and using mass balance. This is best done under conditions where etching is not allowed to occur, as by using an oxidized Si wafer with no externally applied bias to the substrate, to keep the reactant density fixed and avoid the appearance of etch products. In the H-mode of Cl$_2$ ICPs, dissociation to Cl atoms is nearly complete, whereas in the E-mode the fractional density of Cl is very small (18, 26–28). Adding BCl$_3$ to Cl$_2$ increases the Cl$_2$ percent dissociation, likely by passivation of the chamber walls by BCl$_x$ adsorbed on the chamber walls (27), and without actinometric analysis the Cl density is significantly underestimated (29). Use of Cl$_2$/Ar mixtures in etching gives independent control of the rate of chlorination (determined by the Cl flux) and the rate of sputtering (determined by the Cl$^+$ and Ar$^+$ fluxes). Increasing the Ar fraction in Cl$_2$/Ar mixture inductively coupled plasmas content increases the dissociated fraction from 78% to 96% (for 18 mTorr, 10.6 W/cm$^2$) (30) (Figure 1) because of concomitant increases in $T_e$ (21).
Figure 1  Densities of Cl$_2$, Cl, Cl$^+$, and Ar$^+$ in 40% Cl$_2$-60% Ar ICPs (18 mTorr) determined using OES actinometry. Adapted from Reference 30.

Rare gas optical actinometry was able to determine Cl$^+$ and Ar$^+$ densities in Cl$_2$/Ar mixtures ICPs (bright mode) (Figure 1), because emission from excited Cl$^{++}$ and Ar$^{++}$ originated predominantly from electron excited Cl$^+$ and Ar$^+$ and not from a one-step electron ionization and excitation of Cl and Ar (30).

Actinometry determined the densities of Cl, Br, and O, using Ar emission as reference, in Cl$_2$ and HBr high density plasmas to investigate how walls are seasoned during for poly-Si gate etching and affected by CF$_4$/O$_2$ plasma cleaning (31).
SPATIALLY RESOLVED OES Good spatial resolution of the emitted light gives at least a semiquantitative analysis of the emission profiles, as with computerized tomography (CT). OES/CT methods have been combined with laser absorption analyzed by CT (32). The radial and azimuthal CT profiles of the E and H modes in an ICP were found to be very different by OES/CT in CF4/Ar mixtures, as expected (33). Spatially resolved OES/CT methods and time-resolved spectroscopy were combined to compare Ar and O2 plasmas within an rf cycle (34). The oxygen plasma has a much stronger time modulation and a strong radial dependence, making it more difficult to achieve spatial uniformity in it. Combining OES spatial imaging with actinometric methods for quantitative spatial profiles of species densities and electron temperature is just beginning (35). To accommodate the much smaller viewports that are common in commercial reactors, in one study the field of view of the sensor had to be rotated about a point outside the reactor, with concomitant modification of the spatial inversion routine (36).

OES ENDPOINT DETECTION Endpoint detection is extremely important in monitoring the plasma etching of films. Detection is by OE from species formed from etching the film of interest (which will decrease when etching is over) or those from etching the underlying film or substrate (which will increase). This technique is widely used and still being investigated, for example, in etching graded superlattices (37). Most of the advances in endpoint detection are in etching through patterned films with very small, \( \sim 1\% \), openings—and therefore with small OES signals. Improved algorithms for rapidly analyzing optical emission data for several lines are used, with optimized selection of wavelengths and signal analysis techniques such as principal components analysis (38, 39).

Laser-Induced Fluorescence

The strength of laser-induced fluorescence (LIF) is it can measure ground state densities with good spatial resolution. One potential weakness of quantitative LIF is laser saturation. Pulsed laser LIF signals have been corrected for possible saturation by comparing LIF from the species of interest and a stable reference species of known concentration with different laser intensities (40). LIF has been used to monitor CF2 and CF in many studies (22, 41–43) and BCl (44). In one study, absolute F atom concentrations were determined in the afterglow of a pulsed plasma by following the loss of CF2 by \( \text{CF}_2 + \text{F} \rightarrow \text{CF}_3 \) (45). The spatial and temporal profiles of the SiF and SiF2 etch products have also measured by LIF (43, 46, 47). Rotational temperatures of CF and SiF have been determined by LIF (43). Electric fields in argon discharges were made by LIF and laser opto-galvanic (LOG) spectroscopy of Ar atoms (48) and in the sheath above a grooved electrode by LIF of H atoms (49).

The absolute densities of Cl+ and Cl2+ ions in Cl2 etching ICPs were measured by monitoring the intensity of Cl+ LIF—which is proportional to the Cl+ density—and the current from a retractable Langmuir probe—which gives the sum of the
Cl$_2^+$ and Cl$^+$ densities—as a function of rf power (Figure 2) (50, 51). At lower rf powers, in the E-mode, both signals increased with rf power the same way, which suggests that virtually all positive ions were Cl$_2^+$. At higher powers, in the H-mode, the Langmuir current continued to increase with power, while the LIF intensity dropped rapidly, which suggests that the dominant positive ion was Cl$^+$. The densities of O (22, 52), Cl (53), and H (54) atoms have been measured using two-photon LIF in processing plasmas.

Spatially resolved LIF has been used to measure the temperature, density, and radial drift velocity (by Doppler shifts) of metastable Cl and Ar ions in several plasmas (55, 56), and the kinetics of these Cl ions (57). Planar or 2D LIF using a “laser sheet” was used to obtain 2D maps of CF$_2$ to optimize chemical uniformity for etching (58) and chamber cleaning (59) with fluorocarbon/O$_2$ plasmas. This two-dimension LIF imaging method has also been used to study laser ablation of graphite (C$_2$ and C$_3$) for depositing diamond-like films (60) and PLD of YBCO films (61). A high voltage pulse applied synchronously with PLD ablation improved the film hardness of the deposited diamond-like carbon films; the decrease in C$_2$ monitored by LIF suggested an increase in ionic species like C$^+$ and C$^{++}$ that reached the substrate (62).

The “imaging of radicals interacting with surfaces” (IRIS) method monitors LIF from radicals before and after they impinge on a surface, and continues to be
used to determine surface reaction probabilities in CVD and PECVD (63). The reaction probability of SiH on a growing a:Si-H surface was measured to be $\approx 0.96$ (64); that of NH$_2$ was shown to exceed unity in several NH$_3$ mixture plasmas, indicating that NH$_2$ is produced in surface reactions (65); and that of CF$_2$ was shown to depend critically on the fluorocarbon in the plasma and the surface, in some cases indicating etching and in others deposition (66).

**Absorption**

IR absorption to probe vibrational transitions in plasmas and neutral gases is commonly performed using infrared diode laser absorption spectroscopy (IRDLAS) and FTIR spectroscopy. UV/VIS absorption studies often employ hollow cathode lamps of the species of interest (for atomic absorption, AA) and lasers. These give line-integrated densities that are sometimes spatially resolved by computer tomography.

IRDLAS is used to follow reactants and products. Probing the HBr 2-0 band showed that the dissociated fraction of HBr ranged from 25%–60% in an HBr ICP, depending on plasma conditions (67). IRDLAS was used to measure CF$_x$ ($x = 1$–3) densities in a range of studies (68) and to follow CH$_4$ and C$_2$H$_2$ in H$_2$O/CH$_3$OH discharges for diamond PECVD diamond (69).

Ultraviolet absorption has been used to follow the CF$_2$ concentration in numerous fluorocarbon plasmas used for plasma etching and deposition, including in CVD with a polytetrafluoroethylene (PTFE) reactant (70). Absolute densities of CF, CF$_3$, AlF, SiF$_2$, and S$_2$ were measured in reactive gas plasmas by broadband UV absorption spectroscopy (71). The Cl$_2$ density in Cl$_2$ ICPs was measured using the weak 250–400 nm broadband absorption (72); as expected from OES actinometry studies, Cl$_2$ was nearly depleted in high-rf power, low-pressure regimes.

Multivariate analysis was used to separate the broad, overlapping UV absorption profiles of metalorganic and hydride reactants common in III–V growth by MOCVD to control these gas streams (73). A single IR wavelength in the CH stretch mode regime was used to probe composition changes in MOCVD process gases (74); probing in the IR does not induce the photolysis than can accompany UV monitoring.

In addition to using hollow cathode lamps for AA, densities of sputtered atoms have now also been measured using self-absorption of emission lines backreflected into the (magnetron) discharge (75). The chief limitation of lamp absorption is knowing the linewidth of the emission lines from the resonance lamp, whereas that of the self-absorption method is stability and intensity of the reflected light. Self-absorption enables measuring densities of excited state species with lifetimes so long that OES is not possible (metastables or quasimetastables) (76).

Atomic absorption utilizing hollow cathode lamps has become a valuable monitor to control source fluxes in MBE (77, 78), other types of physical deposition such as evaporation, and in PECVD of Si in Si deposition (79). In most early work source density was measured, even though the atomic flux is really the
parameter of interest. The atomic flux can now be obtained by measuring the normal component of the velocity, such as by diode-laser measurements of electron-beam evaporated Y and Ba for the PVD of YBCO superconductors (80). Model independent flux measurements were obtained with a cross-beam scheme, although a simpler counterpropagating beam arrangement provided the flux for symmetric atomic plumes. Frequency-doubled diode lasers were used to detect Al during electron-beam evaporation of Al (81), opening up the possibility of detecting other elements in PVD with such lasers, such as In, Ga, Cu, and Ti.

It is more difficult to detect the nonmetallic atoms important in many thin film processes, such as forming oxides (O for oxidation and epitaxial growth of some oxides) and nitrides (N), etching (F), etc., because ground state absorption in these atoms occurs in the vacuum ultraviolet. This has recently been accomplished for several atoms, such as H (82, 83), N (84), O (85), and F (86–88). For example, the F atom concentration was so determined from a CF$_4$ plasma (86) and this measurement was used to confirm that F atom OES actinometry gives results accurate within a factor of two (87).

In most of these absorption studies, absorption occurs in a single pass through the reactor. In cavity ring-down absorption spectroscopy, the decrease in the Q of a high-finesse optical cavity caused by absorption in the intracavity reactor is sensed; this diagnostic is being used increasingly in thin film processing. For example, Si and SiH (89) and the axial and radial distributions of SiH$_3$ (90, 91) have been measured using cavity ring-down detection during deposition of a-Si:H. Ring-down spectroscopy has been used to measure the absolute densities of other species of interest, such as CH (92), and CF, CF$_2$, AIF, and SiF$_2$ (93).

Other Gas-Phase Probes

An alternative way of measuring the EEDF is by Thomson scattering from the electrons, which can be difficult because of the very weak signals arising from the very small scattering cross section of light from free electrons. The electron density and often non-Maxwellian EEDF are obtained, respectively, from the intensity of collected light and the Doppler broadening caused by electron motion (94, 95). Ion and neutral velocity distributions can also be made with such elastic (Rayleigh) scattering (96, 97).

Nonlinear optical probes (other than two-photon LIF) are only occasionally used in film processing. Degenerate four-wave mixing (DFWM) was used for the first time to probe the laser ablation plume in PLD to overcome difficulties in LIF analysis from the large background light, self absorption, and collisional quenching in the plume (98).

PARTICLES ABOVE AND ON THE WAFER

Particulate formation is a severe problem in CVD, PECVD, sputtering, and plasma etching. In situ monitoring of particles by elastic light scattering [laser light scattering (LLS), Rayleigh scattering] using rastered lasers or laser sheets with video
detection is now widely used as a diagnostic to find process conditions and reactor designs. These designs eliminate the formation of particulates and/or limit their residence near the wafer by either trapping them away from the wafer or directing them into the effluent.

Particle formation from wall flaking is often more important in plasma etching than that from homogeneous processes themselves. The formation and transport path of these flaked particles have been followed in tungsten etch-back processing by LLS in real time (99). In C₆F₆ plasmas, it was deduced that C₂F₄ (measured using FTIR absorption) and not the CFₓ (x = 1–3) radicals (measured by IRDLAS) played an important role in particle formation (100).

LLS showed the formation of particle clouds during the CVD of W from SiH₄/WF₆ mixtures—which leads to roughness of the W films—was caused by unwanted homogeneous processes (101). During MOCVD of AlN, GaN, and Al-GaN, nanoparticles of 35–50 nm diameter are sharply distributed 6 mm above the surface (102). Particle formation has also been shown to be important during several studies of sputtering (103–105). In the laser ablated plume in PLD, particles were detected directly by LLS (106) and by using another laser to decompose them and detect their decomposition products by 2D LIF techniques (107). In situ particle monitors have been developed to be applied to PECVD and poly-Si etching tools (108).

SURFACES AND WALLS

Analyzing the surface with submonolayer resolution is critical in unraveling the reaction mechanism in etching and deposition. The use of optics to probe the surface during epitaxy (epioptics) is now well established (2, 5, 109–112).

Optical analysis of surfaces is feasible when (a) the probe light is confined near the surface (several types of infrared absorption); (b) the symmetry of the surface is lower than that of the wafer, as for broken surface symmetry from surface reconstruction (RDS) or different symmetry properties normal to the surface (second harmonic generation, SHG); (c) the properties and composition of the surface are different or the surface is selectively probed (Raman scattering, IR, p-polarized reflectometry, SE); and (d) the sensitivity of the method is high enough to differentiate between the surface and bulk (SE).

A variety of reflection spectroscopies are commonly used to analyze the film surface and the film itself. They measure \( \frac{r_{xx} - r_{yy}}{r_{xx} + r_{yy}} \) (“usual” normal-angle RDS), \( \frac{r_p - r_s}{r_p + r_s} \) (oblique angle RDS), \( \frac{r_p}{r_s} \) (ellipsometry), and \( R_p, R_s, R_p - R_s \) (all reflectometries); \( R_{p,s} = |r_{p,s}|^2 \) is the (intensity) reflectance and \( r_{p,s} \) is the (electric field) reflection coefficient for p- and s-polarized light. Measuring \( r \) gives phase information absent in measurements of \( R \). “New methods” of oblique angle (as opposed to usual normal angle of incidence) RDS and normal angle (as opposed to usual near pseudo-Brewster angle) ellipsometry are not necessarily new since RDS and ellipsometry are really the same at any angle of incidence. The RDS signal \( \Delta r/r = \frac{r_p - r_s}{r_p + r_s} = \frac{(\rho - 1)}{(\rho + 1)} \), where \( \rho = r_p/r_s \), as measured
in ellipsometry. SE is a valuable probe of multilayer films and the near-surface monolayer-level characterization of composition and is discussed in a later section.

**Reflectance Difference Spectroscopy**

Reflectance difference (or anisotropy) spectroscopy (RDS or RAS) can measure the in-plane surface anisotropy in refractive index $\varepsilon_{xx} - \varepsilon_{yy}$ for (often) isotropic bulk materials in real time (kinetic analysis), usually with the incident and reflected beams near normal incidence. Recent ab initio density functional theory calculations in the local-density approximation suggest that the RDS signal can originate from electronic transitions between surface states, surface and bulk states, and between bulk states that are perturbed by the surface (113–116). Still, the actual interpretation of RDS spectra remains uncertain and so the algorithms needed to use it to control epitaxy are unclear, and often less clear than those for SE.

Early studies using RDS emphasized probing the growth of III–V semiconductor films. Such work has continued, as for GaAs MOCVD (117), and has been extended to monitoring the growth in a range of new materials, including the II–VI semiconductors ZnTe, CdTe, and ZnSe (118, 119) and organics, such as perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) on S-terminated GaAs (120). This last study showed unchanged surface features attributed to bulk GaAs and a feature near 2.3 eV attributed to the HOMO-LUMO gap of PTCDS. Another important development is using RDS to monitor surface doping and estimate the carrier concentration, such as the doping of GaAs(100) by carbon during MOCVD (121) and of ZnTe and CdTe during MBE using N from a plasma source (122). Intra-Mn $d$-level transitions were observed by RDS during epitaxial growth of heavily N-doped ZnMnTe (123). RDS is now being used to monitor the growth of quantum dots, as during the formation of InAs quantum dots and quantum dot stacks (124), and quantum wires, as during the growth of InAs on InP growth for quantum wire formation (125).

RDS is now being used to monitor other processes and properties. During layer-by-layer oxidation of Si(100)-(2 $\times$ 1) surfaces, the half oscillation RDS signal period corresponds to oxidation of 1 ML, making in situ monolayer control possible (126). RDS can monitor ion bombardment of surfaces (127). Anisotropic strain in the film (128–130) and surface electric fields in zinc blende semiconductors caused by Fermi level pinning by surface states (131, 132) can also affect the RDS signal.

**Surface Photoabsorption/p-Polarized Reflectometry**

$p$-polarized reflectometry at oblique angles of incidence is very sensitive to the surface, particularly when probing the alternating cycles of a pulsed (atomic layer) etching or deposition. This is often termed surface photoabsorption (SPA) (above band gap) or $p$-polarized reflectance (below band gap). Methods of extracting surface dielectric functions from SPA data have been developed, with results compared to those from RDS experiments (133).
Pulsed chemical beam epitaxy of GaInP and GaInP/GaP heterostructures on Si(100) has been monitored by \( p \)-polarized reflectometry to enable closed loop control and to monitor surface kinetics (134). Small, fine resolution in the reflectance caused by the alternating of exposures were seen atop the larger, coarser oscillations of interference in the film. SPA has been used to monitor P desorption and adsorption on InP(100) (135), GaN growth (136), and GaAs/AlGaAs heterostructure growth (137). Digital etching of GaAs by pulsed beams of chlorine gas has been investigated using SPA (138). SPA has been extended into the infrared to monitor the vibrational transition in the anisotropic bonding of GaAs nitridation (139). Surfaces can now be probed even for a steady-state process, and with improved sensitivity, by taking the difference between \( p \)- and \( s \)-polarized light, as during strontium titanate homoepitaxy (140).

**Laser Thermal Desorption**

Laser-induced thermal desorption (LITD) of surface layers has been developed to probe surface processes in real-time during plasma etching. Laser-desorbed (LD) species are detected by LIF (LD-LIF) or plasma-induced emission, PIE (LD-PIE). The LD-PIE signal is a transient change in the steady state PIE (OES) emission. The ICP etching of Si by Cl\(_2\) has been investigated by heating the chlorinated surface layer with a XeCl laser (308 nm), using LD-LIF to probe desorbed SiCl (using 308 nm) (141, 142) and LD-PIE to probe Si, SiCl, and SiCl\(_2\) (142). For a given SiCl\(_x\) on the surface, SiCl\(_y\) (\( y \leq x \)) is desorbed. This is directly detected by LD-LIF. For a given desorbed SiCl\(_z\), LD-PIE detects SiCl\(_z\) (\( z \leq y \)); given the energetics of excitation and dissociation there is little fragmentation and mostly SiCl\(_z\) is detected. When plasma conditions (rf power, bias, gas composition) are changed, changes in the LD-LIF signal are proportional to changes in the surface composition; the LD-PIE signal needs to be normalized to reflect changing electron density and, to a lesser degree, \( T_e \). After this correction, the different modes of detection were found to agree with one another. LD-LIF and LD-PIE have also been used to probe the surface during ICP etching of Si by Cl\(_2\)/Ar mixtures (N.C.M. Fuller, D.A. Telesca, V.M. Donnelly, & I.P. Herman, unpublished manuscript). LD-LIF of GeCl at 308 nm has been used to probe ICP etching of Ge by Cl\(_2\) (143).

**Surface and Interface Infrared Absorption**

Fourier transform infrared (FTIR) absorption is surface sensitive when the light is localized to the surface, as in infrared reflection-absorption spectroscopy (IRRAS, IRAS) or attenuated total internal reflection (ATR) spectroscopy, which is usually performed as multiple internal reflection (MIR) spectroscopy in a prism (144). When absorption in conventional prisms is too large for conventional MIR, alternatives are short prisms of the material of interest, transparent prisms coated with the interacting films of interest, or prisms in liquid ambients, for which the angle of incidence is larger than for an air interface (leading to a shorter pathlength due to fewer internal reflections) (145). For Si, this now allows access to low-frequency region
Polarization-modulated infrared reflection (IRRAS) combines the (previously developed) use of a buried metal layer (BML) to enhance the surface electric field and polarization modulation, to study chemistry of materials growth, such as the CVD of Cr₂O₃ (146). Polarization modulation (PM) is used select the weak, yet polarized, response of the surface over the much stronger, yet unpolarized, response of the gas-phase reactants.

The initial adsorption process of SiH₂Cl₂ on Si for Si CVD has been investigated using ATR-MIR (147). For the Si(111)–(7 × 7) surface, no shift in the Si-H stretch dihydride peak is seen from that expected without Cl, suggesting that both Si–Cl bonds in SiH₂Cl₂ are broken before adsorption. For the Si(100)–(2 × 1), the dihydride peak is weak, suggesting that at least one of the two Si–H bonds in SiH₂Cl₂ is dissociated upon adsorption. In a PECVD reactor for depositing a-Si:H, surface hydrides were measured using ATR by comparing the surface before and after the removal of these surface species, by a low density Ar plasma, to differentiate between surface and bulk hydrogen (148); surface hydroxyls were detected during SiO₂ PECVD (149). ATR, along with SE, has been used to follow the formation of silicon nitride films (150) and the growth of BN films (151).

Forming oxides and etching oxides on Si has been studied extensively with IR (and often ATR-MIR) spectroscopy, in investigations closely coupled to density functional cluster calculations of surface geometry and vibrational frequencies. Sometimes, this has been investigated by monitoring the Si–H stretch vibrations by ATR-MIR by FTIR, where slight changes in bonding structure can be discerned on H-passivated Si. Layer-by-layer oxidation by dry oxygen has been shown to occur locally at the SiO₂/Si(111) interface but not at the SiO₂/Si(100) interface (152). In studying the initial stage of the oxidation of H-passivated flat and vicinal Si(111)–(1 × 1) by O₂, oxygen molecules are incorporated into Si–Si bonds without removing surface hydrogen, often at steps (153). The oxidation of Si(100) surfaces by repeated exposures to water vapor and annealing led to the unexpected formation of a silicon epoxide (three-membered Si–O–Si ring) intermediate (Figure 3) (154, 155). Epoxide formation is indicated by the agreement of the observed and calculated Si–O stretching mode frequencies for the III and IV epoxide structures in Figure 3, such as the close agreement of the 969 cm⁻¹ calculated frequency with 965 cm⁻¹ from experiment for Si–O¹⁰ and the agreement of the O¹⁶–O¹⁸ isotope shifts. Ultrathin silicon oxide films grown in acids were seen to contain silicon oxide, carbide, hydride, and hydroxyl species caused by hydrocarbon impurities that dissociated and became permanently incorporated in the film (156). Studies of etching of SiO₂ on Si(100) in dilute hydrofluoric acid have shown that the oxide at the interface is structurally distinct from the overlying oxide and has a different reactivity (145).

These IR methods have been applied to related processes. The first step in nitriding Si surfaces with NH₃ on Si(100)–(2 × 1) was seen to be governed by a complex set of interdimer interactions (157). The initial oxidation of α-SiC(0001)–(3 × 3) occurs through the relaxation of lower layers, away from the surface dangling
Figure 3  IR spectra of the Si(100)-(2 × 1) surface exposed to water and then annealed, using isotopic water. The lower panel shows different cluster structures and their calculated vibrational frequencies for O\(^{16}\) (and for O\(^{18}\) in parentheses), including those for two oxygen epoxide structures: (III) and (IV). Si atoms are gray spheres, O atoms are dark gray spheres, and H atoms are light gray spheres. From Reference 155.

bonds (158); the initial step of Si oxidation occurs at the surface. Studies of the passivation of InP surfaces by different oxides and the etching of these oxides is just beginning (159).

ATR-MIR has also recently been implemented in chlorine-based plasma reactors to monitor the walls (160), in conjunction with OES actinometry of Cl and Cl\(_2\).
(161). Cl atom density increased with time because of the slower atomic recombination on the thin SiO$_2$ films growing on the chamber walls. After striking an SF$_6$/O$_2$ plasma for a short time, the Cl density decreased and this layer was temporarily removed. Silicon oxychloride films were deposited on the reactor walls during Si etching by Cl$_2$/O$_2$, likely through the oxidation of SiCl$_x$ adsorbed on the walls (162), which can be cleaned with SF$_6$ plasmas (163). A B$_2$O$_3$ residue was seen to form on simulated quartz walls in a Cl$_2$/BCl$_3$ ECR plasma reactor (164); the difference in the reflection of $p$- and $s$-polarized light was analyzed to make the measurement more sensitive to the surface.

IR absorption is now being used to probe the buried interface formed during wafer bonding, usually with multiple internal transmission (MIT) spectroscopy (165). In bonding Si wafers initially H-terminated, there is a shift in the Si-H stretching frequency when the surfaces come into contact; this peak disappears after annealing, which demonstrates the formation of Si–Si bonds (165). In bonding oxide termination Si wafers, there are trapped water and hydroxyl groups at the interface that disappear at high $T$, leading to Si–O–Si linkages between the surfaces (165, 166). Similar studies for GaAs wafer bonding show that oxygen plasma treatment of the BSG layer makes a clean, hydrophilic surface (167). The SiH vibrations of implanted hydrogen were followed in the hydrogen-induced exfoliation of silicon (168).

**Surface Morphology**

LLS is now frequently used to investigate surface roughness that can originate during deposition from the creation of quantum dots; the formation of misfit dislocations; and roughening caused by preferential growth associated with dislocations, such as during (169) and after (170) the growth of InGaAs/GaAs. LLS was combined with laser stress measurements to follow the relaxation and morphological evolution of InGaAs/GaAs by MBE (171). Spectroscopic light scattering has also been used to measure thin film evolution and surface morphology in real time during the growth of SiGe on Si (172).

**Other Surface Sensitive Methods**

Raman scattering can have monolayer sensitivity for analysis, as during growth of GaN (173), CdS, and ZnSe, and the nitridation of GaAs (174). The growth of PTCDA by organic molecular beam deposition on GaAs and Si has been monitored by Raman spectroscopy (175). Changes in GaAs bands and PTCDA internal and external vibrational modes indicated interface formation (176).

Second harmonic generation (SHG) is sensitive to surfaces and interfaces when the bulk is centrosymmetric (177). It has been used recently to study the initial steps of Si etching by chlorine (178), Si (179) and SiGe (180) deposition, and Si oxidation by ozone and oxygen (181). SHG imaging has also been demonstrated (182).

Infrared-visible sum frequency generation (SFG) has been used to probe vibrations of species on surfaces or of films, with minimal interference from thermal
emission or the gas phase (183, 184), and in related studies of catalysis at high pressure (185) and polymers (186). SFG during diamond deposition suggests that there is CH at the surface, but no detectable steady-state CH$_3$ (187).

Photoemission is very sensitive to the state of the surface. Layer thickness can be monitored by oscillations in the photoemission due to the growth of individual layers (188), as can surface reconstruction (189).

**FILMS**

Reflection-based methods are widely used to study growth and etching rates, the composition of growing films, and substrate temperature during deposition.

**Reflectometry**

Growth rates and optical constants can now be extracted from in situ multi-wavelength normal incidence spectroscopic reflectance of growing films and multilayer film structures, such as by MOCVD and MBE, by using a virtual interface model (190); in this way the cumulative errors in standard multiple-layer models are avoided for good real-time control. The spectroscopic nature of this interference measurement yields enough accuracy so that more complex methods, such as SE, are often not needed, as in controlled growth of a vertical cavity surface emitting laser (VCSEL) (191).

Such methods are being more widely adopted in academic laboratories, national laboratories, and in some development manufacturing deposition tools (191, 192). Reflectance with virtual interface modeling is currently used on every MOCVD and MBE machine at Sandia National Laboratory (Albuquerque, NM) to improve yield (W. Breiland, private communication). Although it is not yet widely used in industry, interferometric endpoint detection is now routinely used in Si gate etching in new industrial tools, mostly in an empirical mode. There is much work remaining in algorithms for patterned structures, and these techniques are gaining increasing usage (R. Gottscho, private communication).

Reflectance was used to measure the thickness of the diffusion barrier layers Ti and TiN (193). Reflection interferometry has been used to monitor the growth and etching of C-doped GaAs on GaAs caused by the slightly different refractive index of the doped layer (194) and plasma (195) and wet (196) etching of Si. Dual wavelength interferometry has also been used to control plasma etching of transparent materials, such as SiO$_2$ (197). The densities of etch radicals C and F were also obtained with Xe and Ar OES actinometry and used as inputs to an etch rate model for model-based real-time control.

Laser reflectometry gives process rates and a means of endpoint detection, as during the etching of magnetic Pt/Co and Cu/Co multilayer structures (198). It can be used to map etch rates via changing film interference, and can do so simultaneously across a wafer to aim for etch uniformity and endpoint control (197, 199), including full wafer monitoring with CCD cameras (200). The use of multiple
wavelengths improves the accuracy and helps differentiate between etching and deposition. Speed and accuracy were improved over conventional in situ reflectometry methods, such as peak/valley counting, by using the nonlinear estimation technique common in systems theory, extended Kalman filtering (EKF) (201).

Interference reflectometry has also been used for monitoring and endpoint control in patterned processing, including the selected area GaAs MOCVD (202), Si$_3$N$_4$ etching and localized oxidation of silicon (LOCOS) (203), deep RIE etching of GaAs/AlGaAs Bragg mirror VCSEL structures (204), and SF$_6$ ICP plasma etching of polysilicon as a function of aspect ratio (205).

A related method is pyrometric interferometry, for which the substrate temperature $T$ is otherwise regulated and the temperature obtained from uncorrected pyrometry measurement is monitored. This leads to an oscillating effective “pyrometric $T$” (which is what $T$ would be if the emissivity were not changing) during the growth of layers, as $R$ oscillates because of interference. This has been used recently to monitor the MBE growth rates and composition of InAlAs/InGaAs (206) and AlGaN/GaN (207) quantum well structures. Growth of GaN in a Ga-rich regime can produce surfaces that are mirror-like or covered with Ga droplets, which is seen as a continuous decrease of the “pyrometric $T$” averaged over a fringe because of this increase in $R$ and the decrease in emissivity (207).

Two-channel spectroscopic reflectometry (2CSR) was developed to obtain $R_p$ and $R_s$, and applied to in situ monitoring of uniform and patterned structures during RIE (208). Light was polarized by a Glan-Taylor prism and incident near the pseudo-Brewster angle, and the $p$ and $s$ components of the reflected beam were physically separated with a Wollaston prism. This method gathers more information than normal incidence reflectometry, but less than SE.

Broadband visible reflection has been used to determine the endpoint for a variety of chemical mechanical planarization (or polishing) (CMP) processes (209). Whereas large changes of reflectance are expected when the bulk of the metal is removed after CMP, leaving metal only in vias, the thickness of underlying dielectric can still affect the endpoint signal and analysis.

Scanning probe microscopy is rarely used in situ during film processing, for obvious reasons; still, some applications are possible. With a fiber-based near-field (reflectometry) microscope at 3 $\mu$m, chemically amplified polymer photoresists were patterned by ultraviolet radiation and then imaged near the OH band of the polymer (210). This region is sensitive to photochemical changes associated with latent image formation.

**Ellipsometry**

Reflection ellipsometry gives $\rho = r_p/r_s$ or $\rho = \tan(\Psi) \exp(i\Delta)$. Real-time SE is now a well-established monitor of growth, and is increasingly being used to control growth (2, 110, 211) with new numerical algorithms, such as the virtual-substrate approximation in virutal interface theory (212), to obtain the near-surface dielectric function. Rapid reliable information is now becoming routine by using parallel spectroscopic detection (for spectroscopic or multiwavelength analysis),
realistic models of the films (including surface and interface roughness and composition uncertainties), and efficient analysis algorithms. Progress in developing and implementing real-time SE has progressed on a range of materials and processes (112, 213–218), and is expected to continue even deeper in the UV (to the VUV, for photoresists and optical coatings) and the IR (to the mid- and far IR, for phonons and free carriers). In fact, IR SE, which gives sensitivity to vibrations, has been used for real-time analysis of growth (219). This provides chemical information about C-H bonding in the PECVD of a-C:H (220) and plasma etching of Si (221).

Real-time SE was used to follow the early stages of GaP MOCVD on Si(100) and GaAs(100) (222) in a study that illustrates the importance of materials modeling. For Si(100), these data were successfully modeled with the GaP and Si interpenetrating over the first 75 Å, and then the GaP was characterized as bulk GaP with 3–5% voids (Figure 4). This work also illustrates the potential for using SE for

Figure 4  The trajectory of the imaginary versus real part of the pseudodielectric function at 3.59 eV for growth of GaP on Si, with experimental data (open circles) and model predictions for the different phases of growth, as depicted on the right. (The pseudodielectric function is a representation of the ellipsometry data assuming a model with an ideal, flat semi-infinite medium in vacuum.) From Reference 222.
surface temperature measurements, with the Si temperature determined to a precision of ±1°C. The importance of modeling in SE is seen in the deposition of BN films, which has been modeled in terms of two-layer (223) and less-conventional three-layer models (224,225), and in the real-time high-resolution depth profiling of compositionally graded a-SiC:H graded during CVD (226), where a four-medium virtual interface approximation gave the near-surface C content, as well as the growth rate and surface roughness.

Ellipsometry has been used to determine growth mechanisms and sometimes control the growth of many semiconductors, including microcrystalline Si (227), SiGe (228), GaN (229), and AlAs (230), and that of InGaAs quantum dots stacks (231). Several recent studies have demonstrated the ability of SE for closed-loop control of the composition of ternary alloys during deposition (MBE, MOCVD, etc.), such as the composition fraction x in Hg1–x,CdxTe (232), In1–x,GaxAs (233), In1–x,GaxAs (234), and In1–xAlxAs (235). Composition control is also the goal in monitoring the growth of varying refractive-index profiles (236).

The thickness of sputtered thin metal films and multilayer x-ray mirrors has been determined using in situ SE for Au, Pt, Pd, Rh, Cr, Cu, W, and C (237).

Real-time and other in situ SE studies has been used to control growth of many insulators, such as Y2O3 (78), SiO2/Si3N4 multilayers and SiOxNy gradient-index coatings (238), Nb2O5 (239), BaSrTiO3 (240, 241), and diamond films (uniformity issues) (242).

Real-time SE has also been used to control thickness and etch rate in a commercial ICP reactor using careful in situ design of experiments methods (ISDOE) and EKF filtering (243, 244). Other groups used SE for real-time feedback control of thermal chlorine etching of GaAs and plasma etching of silicon nitride films (245), and control of wet etching of GaAs/AlGaAs (246). SE analysis during etching of patterned films is becoming evermore important (247, 248), including that of poly-Si gates (247), TiN and polysilicon (249), and GaAs (250). The same characteristic ellipsometric signature was seen as for unpatterned films, suggesting potential for process control. SE is becoming a valuable in situ monitor of critical dimensions (beyond just feature depth); in one study, this was optimized at normal incidence (and so it was really RDS) (251).

Analysis of modified surface layers is another goal for SE. Real-time SE has been used to assess the preparation of smooth and abrupt interfaces by removing ∼0.4–5 nm of the overlayer by wet chemical treatments, in GaN, AlN, and AlGaAs (252) and 4H-SiC (253). SE is also commonly used to monitor surface layers during plasma etching, such as in Cl2 plasma etching where the interfacial region was modeled as two layers: a mixture of a-Si, c-Si, and SiClx, and a layer of a-Si and SiClx on top (254). The CVD of fluoroalkylsilane monolayer films to improve the adhesion control in microelectromechanical systems (MEMS) (255) has also been monitored by SE.

SE is now used to probe other types of processes, such as wet and dry oxidation of copper (256), plasma nitriding of GaAs surfaces to form GaN (257), and forming phases during the fabrication of nickel silicide films (258), and to
measure properties, such as the photogenerated carrier density during the PECVD of microcrystalline Si (259).

Other Film Diagnostic Needs and Processes

**FILM AND WAFER TEMPERATURE** Tight control of wafer temperature is often essential (1, 3). For example, temperature control of ±1°C during MOCVD is needed to keep the InGaAsP bandgap within ±4 nm near 1550 nm (260). Reflectometry and SE, and other optical probes, such as pyrometry, are being used increasingly for noncontact thermometry of wafers. In pyrometry, the main uncertainty is the emissivity \( \varepsilon(\lambda, T) \), which equals \( 1 - R(\lambda, T) - T(\lambda, T) \) \( R \) is (intensity) reflectance, \( T \) is (intensity) transmittance, since \( R \) depends critically on the films atop the wafer (even for \( T = 0 \) opaque wafers). Emissivity corrections during growth have been made using real-time reflectance in several studies (260, 261). One current challenge is pyrometry during AlGaN growth on sapphire or SiC substrates, because the substrates are transparent in the visible (W. Breiland, private communication).

Diffuse reflectance spectroscopy (DRS) measures the temperature-dependent change in near-bandgap light transmitted through a wafer, diffusely reflected by the wafer backside and transmitted through the top of the wafer, and has been used to measure and control temperature as precisely as ±0.5°C during the growth of several ternary III–V semiconductors (77, 234, 262, 263). An algorithm has been developed that corrects for the distortions in the band-edge profile from interference and/or absorption in the growing epilayer (264). Because such DRS is not possible when depositing a smaller band gap material atop a larger one, DRS has been performed by reflecting light from the backside off of a reflecting layer that was deposited first (265).

**FILM STRESS** In situ measurement of film stress during deposition has been performed on wafers by the reflection of at least two laser beams from the wafer, and relating the so-determined wafer curvature to stress by using Stoney’s equation. In the new multiple-beam optical stress sensor, a solid state laser is sent through an etalon to produce three to five parallel beams and the spacing of the reflected beams is tracked with a CCD camera to determine wafer curvature (266). This was used to examine stress evolution and relaxation during growth (266–268). Stress has also been determined by monitoring laser beam deflection from cantilevers, as during BN deposition (269) and InAs MBE for quantum wire formation, using shaped substrates oriented in different directions (270).

**SURFACE LIGANDS DURING NANOCRYSTAL FILM FORMATION** The deposition of thin films of nanoparticles by the evaporation of the solvent (dry casting) has been probed in real time using MIR ATR. In forming films of CdSe nanocrystals capped on the surface with pyridine and initially dissolved in pyridine, the 1436.1 cm\(^{-1}\) vibration of the pyridine solvent is seen to disappear in ∼20 min (Figure 5) when
Figure 5 Monitoring the formation of thin films of CdSe nanocrystals capped on the surface with pyridine, by following the 1436.1 cm\(^{-1}\) vibration of the pyridine solvent and the shifted peak of pyridine ligands at 1445.2 cm\(^{-1}\) bound to the nanocrystal surface. Adapted from Reference 271.

the film is dry (271). The shifted peak of pyridine ligands on the nanocrystals at 1445.2 cm\(^{-1}\) initially increases as the density of nanocrystals near the surface increases during evaporation, and then slowly decreases. This indicates that much of the nanocrystal cap is desorbing (which is not surprising for the weakly bound pyridine); only about one third of the cap molecules remain after 3 days.

OTHER FILM DIAGNOSTICS Scatterometry is monitoring diffraction from a periodically patterned film or substrate to infer the topography of the surface (feature height, width, sidewall angle/shape); it is formally the same as LLS described above for surface morphology analysis. It is continuing to be developed (272–274), and is fast becoming mainstream for critical dimension (CD) and thin film measurements. The CD metrology capabilities of scatterometry rival those of SEM, and are being used increasingly in manufacturing. Still, more work needs to be done on extracting profile shapes from scatterometry (R. Gottscho, private communication).

Whole wafer fluorescence imaging was developed for on-wafer spectrofluorometric evaluation of the photoacid generator compounds that are used to
chemically amplify (accelerate) photoresists by doping the resist with pH-sensitive fluorophores (275).

CLOSING COMMENTS

The application of these optical probes to film processing is fairly mature in that most developed spectroscopies have already been applied to help understand these processes. Future developments include the use of these diagnostics to understand and control new film processes and the continued utilization of newly invented optical spectroscopies in thin film processing science.

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LITERATURE CITED

19. Malyshev MV, Donnelly VM, Downey
169. Pinnington T, Lavoie C, Tiedje T, Have- 
79:1698–701
170. Gonzalez MU, Sanchez-Gil JA, Gonzalez 
171. Gonzalez MU, Gonzalez Y, Gonzalez L. 
172. Chason E, Sinclair MB, Floro JA, Hunter 
72:3276–78
276–82
175. Kampen TU, Tenne DA, Park S, Salvan G, 
Solidi B 215:431–34
176. Salvan G, Tenne DA, Kampen TU, Scholz R, 
179:113–17
Technol. A 16:3029–33
179. Hu XF, Xu Z, Lim D, Downer MC, Parkin- 
71:1376–78
180. Mantese L, Selinidis K, Wilson PT, Lim 
154:229–37
181. Nakamura K, Kurokawa A, Ichimura S. 
182. Florsheimer M, Bosch M, Brillert C, 
Technol. B 15:1564–68
183. Shen YR. 2001. Pure Appl. Chem. 73: 
1589–98
186. Chason E, Sinclair MB, Floro JA, Hunter 
72:3276–78
276–82
189. Zinck JJ, Ross RS, Owen JHG, Barvosa– 
Phys. Lett. 79:2354–56
Phys. 78:6726–36
191. Breiland WG, Hou HQ, Chui HC, 
174:564–71
192. Breiland WG, Coltrin ME, Creighton JR, 
Hou HQ, Moffat HK, Tsao JY. 1999. 
194. Rebey A, El Jari B, Leycuras A, Laugt S, 
195. Benson TE, Kamlet LI, Ruegsegger SM, 
196. Steinsland E, Finstad T, Hanneborg A. 
197. Sarfaty M, Baum C, Harper M, Her- 
198. Khamsehpour B, Wilkinson CDW, Chap- 
15:2069–73
199. Wong K, Boning DS, Sawin HH, Butler 
A 15:1403–8
200. Pendharkar SV, Resnick DJ, Dauksher 
WJ, Cummings KD, Tepermeister I, Con- 
15:816–19
201. Vincent TL, Khargonekar PP, Terry FL. 
10:42–51
203. Layadi N, Molloy SJ, Esry TC, Lill T, 
B 17:2630–37
204. Moussa H, Daneau R, Meriadeck C, Manin 
L, Sagnes I, Raj R. 2002. J. Vac. Sci. Tech- 
nol. A 20:748–53
Cryst. Growth 175:256–61
245. Rosen IG, Parent T, Fidan B, Wang CM,
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