Pure & Appl. Chem., Vol. 70, No. 6, pp. 1181–1186, 1998.
Printed in Great Britain.
© 1998 IUPAC

Plasma–surface interactions in the processing of III–V semiconductor materials

M. Losurdo, P. Capezzuto, G. Bruno

Plasma Chemistry Research Center - CNR-MITER via Orabona, 4 - 70126 Bari, Italy

Abstract: Surface modifications of InP and GaAs semiconductors induced by the interaction with H_2, N_2 and O_2 plasmas are investigated in situ and in real time by ellipsometry. It will be shown that: (a) the kinetic ellipsometry allows to define the "border line" between the cleaning (oxide removal) and damage (phosphorus depletion) processes of InP which can occurr during exposure to H atoms; (b) electronic phenomena at the GaAs/oxide interface play an important role in the oxidation kinetics; (c) the self-limiting kinetics of GaAs nitridation is due to the slow out-diffusion of As.

INTRODUCTION

Although the developments in the field of low pressure plasmas mainly deal with industrial applications based on heterogeneous solid-plasma systems, the knowledge of the plasma-surface interactions is still behind that of the "more important" plasma phase processes. The situation reflects the fact that plasma chemistry researchers have been attracted, hystorically, by the complex and exciting phenomena occurring in the plasma phase leaving the comprehension of the "less important" plasma-surface processes to the empirism and art of technologists. In these last years, however, it has been growing the convinction that further progress in the application fields can be obtained only through the understanding of the fundamental problems. Among these, the kinetics and chemistry of the surface modifications, also including morphology and structure, are important and complex themes which need further fundamental research work.

The complexity of understanding the plasma-surface interaction arises from the variety of species interacting with surface and of related phenomena which control the composition, the morphology, the structural properties and the thickness of the surface layer. Among many factors contributing to such a complexity, the lack of in situ diagnostic techniques able to fingerprint the surface during the plasma treatment has certainly been one of the main causes. In fact, well established surfaces diagnostics, such as X-ray photoelectron spectroscopy (XPS), Auger Spectroscopy (AES) and reflection high energy electron diffraction (RHEED), are mainly used in ex situ configuration, as they operate under ultrahigh vacuum operative conditions. In recent years, the development of in situ real time is becoming determinant, and several optical techniques have been developed, whose application is compatible with the treatment and growth environment of III-V materials. Among others, spectroscopic ellipsometry is very suitable to monitor in situ and in real time surface modifications because of its nondestructive character and high sensitivity to surface chemistry and control of layer thickness with submonolayer resolution.

In the present paper, we report on the interaction processes of (a) hydrogen plasmas with InP surfaces for the native oxide removal; emphasis is given to the role of surface temperature on surface chemistry and kinetics, (b) oxygen plasmas with GaAs surfaces for the plasma anodization; the initial oxidation kinetics and the effect of UV light irradiation is focused, and (c) nitrogen plasmas with GaAs surfaces for the nitridation process to give thin GaN layers; we formulate problems related to the self-limiting kinetics of nitridation. Ellipsometry, in both spectroscopic and kinetic mode, is used to monitor in situ and in real time the surface modifications. It will be shown that: (a) the kinetic ellipsometry allows to define the "border line" between the cleaning (oxide removal) and damage (phosphorus depletion) processes of InP which can occurr during exposure to H atoms; (b) electronic phenomena at the GaAs/oxide interface play an important role in the oxidation kinetics; (c) the self-limiting kinetics of GaAs nitridation is due to the slow out-diffusion of As.

IN SITU REAL TIME DIAGNOSTIC OF PLASMA-SURFACE INTERACTION: ELLIPSOMETRY

The recent advances in microelectronics and optoelectronics requiring precise control of thicknesses, of the composition and morphology of epitaxial semiconductor layers, pushed the use of optical technique for the real time monitoring of surface modifications and, in particular, of reflection ellipsometry.
Books (ref. 1,2) and recent reviews (ref. 3,4) report on the principles on which the reflection ellipsometry is based and it is not our intention to give here a rough summary of them. This paragraph rather intends to explain briefly what reflection ellipsometry masures and how it applies to III-V semiconductors diagnostics

Reflection ellipsometry measures the modification of the polarization state of a light beam upon reflection from an optically active medium. The ellipsometric angles Ψ and Δ measure the amplitude change ($\tan\Psi = |r_p|/|r_s|$) and phase shift ($\Delta = \delta_p - \delta_s$) of the components of the polarized light parallel, r_p, and perpendicular, r_s, to the plane of incidence. From Ψ and Δ, the ratio, $\rho = r_p / r_s = tg\Psi \cdot e^{i\Delta}$ is calculated, and the pseudodielectric function, $\langle\varepsilon\rangle$, for a complex, film-covered surface is derived by the expression:

$$\langle\varepsilon\rangle = \langle\varepsilon_1\rangle + i\langle\varepsilon_2\rangle = \varepsilon_0 \cdot tg^2\Phi_0\left[1 + sin^2\Phi_0 \frac{(1-\rho)^2}{(1+\rho)^2}\right] \quad (1)$$

The angles Ψ and Δ can be acquired as a function of energy in the range 1.5 - 5.5 eV (spectroscopic ellipsometry, SE) or as a function of process time at a fixed energy (single wavelenght ellipsometry, SWE). Although the measure is simple, but not easy, extremely delicate is the interpretation of the ellipsometric data, in terms of surface and material properties. The analysis of the SE spectra and kinetic profiles is based on the use of optical models, which need, in some cases, to be confirmed by other experimental data. The commonly used optical models are based on the Bruggemann effective medium approximation (BEMA) (ref.5). It assumes that inhomogeneus layers have a dielectric function deriving from the dielectric functions of the individual components, since each of them retains its original dielectric response. The parameters of a BEMA model are usually the volume fractions of the constituents and the layer thickness.

An example of the surface chemistry sensitivity and of the potentiality of the in situ ellipsometry for process kinetics monitoring is shown in fig. 1. Figure 1a shows the time dependence of the imaginary part of the pseudodielectric function, $<\varepsilon_2>$, during the exposure of a GaAs surface to a hydrogen plasma, for the native oxide removal, and, sequentially, to a nitrogen plasma for the GaAs nitridation. The corresponding layer thickness profiles, as derived by modelling, are also shown. SE spectra shown in fig.1b have been acquired at the significant points A-C of fig. 1a and the corresponding BEMA models are also shown. Thus, the following surface chemistry can be described: the removal of oxygen from a GaAs crystalline substrate covered by 25 Å of native GaAs oxide (point A) to obtain a less dense and microrough GaAs surface layer (point B), and the subsequent nitridation (line BC) to form a 40 Å GaN layer (point C).

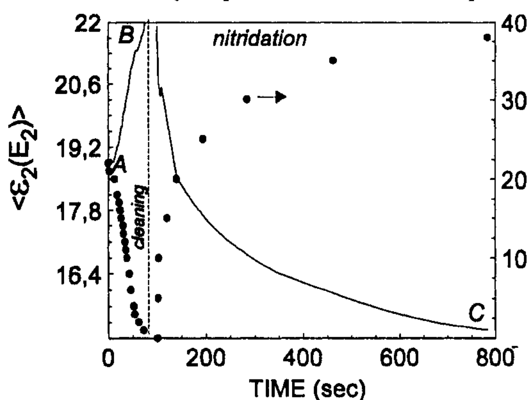

Fig.1a. $<\varepsilon_2>$ vs process time during GaAs exposure to a H_2 plasma (AB line) for oxide removal and to a N_2 plasma (BC line) for nitridation. Full points are for the corresponding GaAs oxide and GaN thicknesses.
(H_2 plasma: 1000 sccm, 1 torr, 60 watt, 230 °C; N_2 plasma: 100 sccm, 0.2 torr, 200 watt, 250°C)

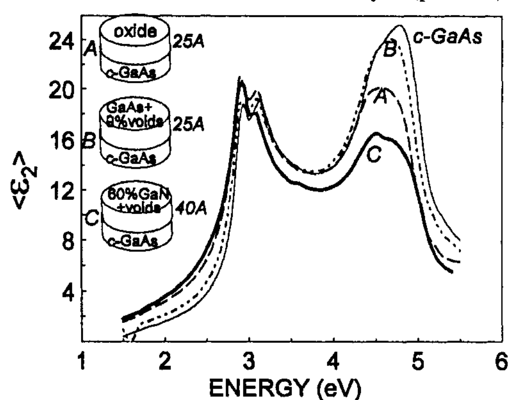

Fig. 1b. SE spectra acquired (A) before plasma treatment, (B) after oxide removal by H2 plasma and (C) after nitridation. The corresponding best fit BEMA models describing the chemistry and morphology of the surfaces are also shown. The SE reference spectrum of the c-GaAs is shown for comparison.

HYDROGEN PLASMA FOR III-V SURFACES CLEANING: ROLE OF TEMPERATURE ON SURFACE CHEMISTRY AND KINETICS.

The interaction of H atoms with III-V semiconductor surfaces is attractive, since atomic hydrogen can efficiently reduce carbon contaminations and native oxide (ref.6,7), giving good-quality III-V surfaces for epitaxial growth. In addition, H atoms act on the material by passivating various kinds of defects and, hence, reducing the surface and bulk density of states (ref.8). However, it is well documented (ref.9) that H atoms can also induce damage of III-V surfaces. In particular, for InP surfaces, the interaction with H atoms results in the competition between the removal of the native oxide (the cleaning process)

$$InPO_x + 2x\ H \rightarrow InP + x\ H_2O \qquad (2)$$

and the selective depletion of the V-group element, (the damage process)

$$InP + 3\ H \rightarrow In + PH_3\uparrow \qquad (3)$$

which causes material damage.
Similar processes occur for GaAs surfaces interacting with H atoms, where in addition the ablation of both III- and V-group elements (the etching process)

$$GaAs + 6H \rightarrow GaH_3 + AsH_3 \qquad (4)$$

is also effective (ref. 10).
The relative importance of the above processes strongly depends on plasma parameters, and on surface related parameters, such as morphology, crystallographic orientation and temperature. Among all these parameters, the surface temperature is the key to control and select the overall surface chemistry and kinetics. In fact, the occurrance of the above processes (eqs. 2-4) is descriminated by the different temperature dependence of the reaction rates as can be derived by the like-Arrhenius plot shown in fig. 2 for InP surface-H atom interaction. In the figure, the O-removal rate and P-depletion rate are plotted *vs* temperature in the range 25°C - 350°C. The O-removal rate, $r_{ox}=\Delta ox/\Delta t$, has been evaluated from the linear time dependence of the oxide thickness obtained according to the ellipsometric approach described previously. Analogously, the P-depletion rate, $r_P = \Delta V(In+voids)/\Delta t$ has been derived by the time variation of the volume fraction of indium+voids as induced by the H atom interaction and measured through modelling of the real time SE spectra (ref. 6). The qualitative behaviour of these kinetic data is consistent with the experimental observation that at 250°C, where the P-depletion rate is at its minimum, the overall surface process results in the selective removal of oxygen.

Also, the quantitative evaluation of the pseudo activation energy, E_a*, gives for the O-removal process the value of 0.20±0.05 eV; whereas, the P-depletion process is characterized by two values of pseudo-activation energy, depending on temperature: a negative value of -0.15±0.05 eV in the low temperature range 25 - 200°C, and a positive value of 0.20±0.05 eV in the high temperature range 200 - 350°C. The interpretation of these E_a* data is straightforward when it is considered that chemical reactions at solid surfaces usually are described by the following sequence of events: the chemisorption of atoms/radicals on active sites, the chemical reaction, and the desorption of the reaction products. Therefore, the chemical schemes corresponding to the O-removal and P-depletion processes has been written as shown in fig. 2.

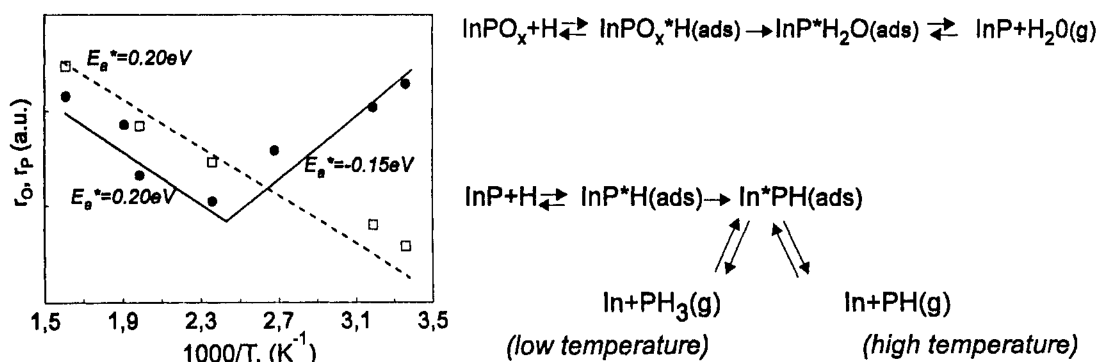

Fig. 2. Reaction scheme for the InP oxide removal and phosphorus depletion processs by H2 plasma. On the left, the O-removal rate, rO, and P-depletion rate ,rP are reported in Arrhenius-like plot. (H_2 plasma: 1000 sccm, 1 torr, 60 watt)

Specifically, the fact that the P-depletion presents two different thermal activation zones is explained on the basis of two different species desorbing from the InP surface, similarly to what is reported for the etching of GaAs by Cl_2 plasmas (ref. 11). At high temperature (positive pseudoactivation energy), the surface is sparsely covered by H atoms, and, hence, PH (which has a positive desorption heat) is formed and desorbes; whereas, at low temperature (negative pseudoactivation energy), the surface is well covered by H atoms and PH_3 (which has a negative desorption heat) (ref. 6) is formed and easily desorbes.

OXYGEN PLASMAS FOR GaAs OXIDATION: ELECTRONIC PHENOMENA AT THE OXIDE/GaAs INTERFACE

The GaAs plasma anodization is a good representation of the complexity of plasma surface interactions, as in this case the surface chemistry and kinetics are affected, besides by the surface temperature, also by electronic phenomena at the semiconductor surface. In particular, the transport of oxidizing species through the surface layers is enhanced by the existence of strong electric field across the oxide film. The foundation for understanding the growth of oxide layers by plasma anodization have been laid by Cabrera and Mott (ref. 12). It is now well established that the oxidation rate is dominated by an electric field assisted motion of either cations or anions (ref.13,14) through the oxide layers and that, for thicker oxides, linear-parabolic kinetics are often observed (ref.15). However, in spite of the large number of experimental works (ref. 13-17), the foundamental understanding of the initial oxidation kinetics, i.e. the growth of the first few hundreds Angstrom is very poor. In the initial oxidation kinetics, electronic phenomena have an important role, since they considerably affect the electronic structure of the semiconductor, the charge distribution at the surface/interface and, consequently, the gas-surface interaction. The existence of electronic phenomena affecting the GaAs oxidation kinetics has been evidenced by the doping effect recently reported by Irene (ref.18) and by the visible and UV light irradiation of the GaAs surface (ref.19,20).

The role of UV light irradiation on the plasma-surface interaction has been investigated, in the past, by Bruno et al (ref.21), during the deposition of a-Si:H films. In this case, a chemisorption photoenhancement has been invoked to explain the increase of deposition rate. More complex is the effect of UV light irradiation on GaAs plasma anodization kinetics, and contradictory hypotheses have been reported (ref. 19,20,22). However, the recurrent explanation is that the UV light irradiation acts to increase the density of active oxygen atoms in the gas phase and, hence, on the surface (ref. 19). Winters et al (ref. 23) investigated the effect of UV light irradiation on the c-Si etching, and introduced the idea that UV light activates phenomena at interfaces; they stated that "UV-light causes the Fermi-level to move toward the conduction band, i.e. approaches the flat band situation, and, hence, increases the electric field at the interface". However, they did not exclude other effects of UV-light. We took on board the Winters' idea and, by the investigation of the joined effect of UV light irradiation and GaAs crystallographic orientation, we evidenced the important role of electronic phenomena occurring at the GaAs/oxide interface in controlling the oxidation kinetics. Figure 3 shows the GaAs oxide thickness profiles obtained for oxidation performed with and without UV light irradiation, and at different cristallographic orientation of GaAs.

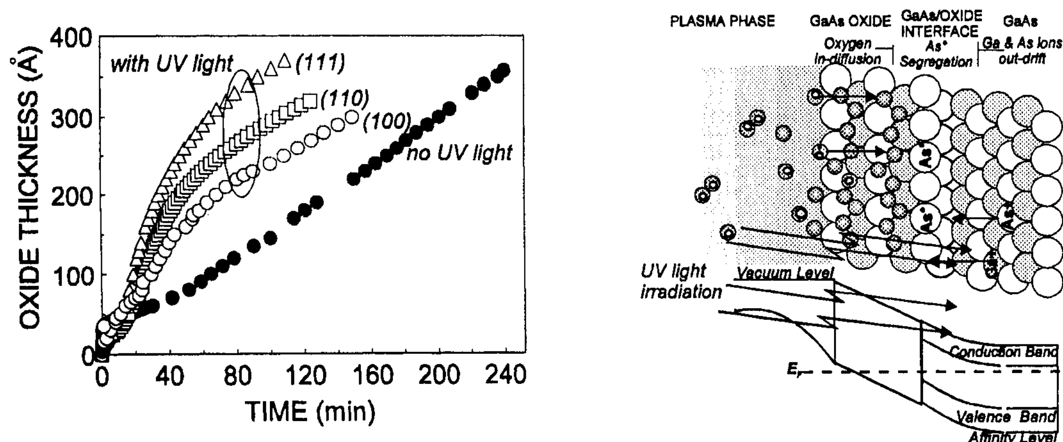

Fig.3. Thickness of GaAs oxide layers grown on GaAs substrates with (100), (110) and (111) crystal orientations during plasma oxidation with and without UV light irradiation. The scheme on the right evidences the main processes occurring at the oxide/GaAs interface. The band bending at the interface is also shown. (O_2 plasma: 10 sccm, 70 mtorr, 100 watt, 130 °C).

A photoenhancement of the oxidation rate is observed for oxide thickness lower than 250 Å. Depending on oxide thickness, the photoeffect estinguishes according to the Lambert-Beer law (ref. 24), and for oxide layer thicker than 250 Å, oxidation with and without UV light irradiation proceeds with the same rate. Also, the photoenhancement depends on the GaAs surface orientation. The anisotropy of the photoeffect and its Lambert-Beer law dependence clearly evidence that UV light is absorbed by the oxide layer and at the GaAs surface. Here, UV photons of sufficient energy can promote the GaAs photoionization process and, hence, the ion migration toward the surface, as illustrated in the scheme of fig. 3. Finally, the lower ionization threshold energy (ref. 25) for the GaAs(111) orientation is responsible for its oxidation rate value higher than that obtained for other orientations.

NYTROGEN PLASMAS FOR GaAs NITRIDATION: SELF-LIMITING KINETICS

Nitridation of GaAs is of considerable interest from both technological and scientific points of view. From the technological point of view, thin GaN layers are used for the encapsulation and passivation (ref. 26) of III-V semiconductors and as "buffer" layer in the epitaxial growth of GaN layer on GaAs substrates (ref. 27). From the scientific point of view, the nitridation process presents open questions related to its self-limited kinetics which impedes the growth of thick GaN layers (ref. 28). The self-limiting nature of the nitridation process has also been reported for Si (ref. 29) and explained by the very small diffusivity of nitridating specie in the barrier layer of silicon nitride. More complex is the origin of the self-limiting nitridation kinetics of the composite GaAs semiconductor, because of the competition of Ga and As atoms to react with N atoms and of the out-diffusion of As and/or AsN_x species which could also be a limiting step in the nitridation. With respect to this, the in situ diagnostics of the surface kinetics by ellipsometry assumes noticeable importance, as nitridation kinetics and chemistry can be clarified and suggestions on how to enhance the nitridation depth can be formulated.

Figure 4 shows some typical kinetic profiles for GaAs nitridation by N_2 and N_2/H_2 (r.f.) plasmas at various surface temperatures. In the figure, the GaN thickness values have been derived by modelling the ellipsometric traces with a two-layer model which includes a GaN outmost layer and an As-rich GaN/GaAs interface layer (ref. 30). The nitridation depth is limited to few tens of Angstrom for N_2 plasma nitridation, whereas N_2/H_2 plasmas give nitrided layers as thick as 140 Å. Also, the GaN layer thickness depends on temperature, whose upper limit is the GaAs decomposition temperature (550 °C); at temperature higher than 550°C, the GaN layer is very rough and Ga-rich (ref. 30). Thus, the low nitridation depth obtained by N_2 plasmas can be explained by the As segregation which acts as antidiffusion barrier for nitrogen atoms. The increase of the nitridation depth by hydrogen addition to nitrogen plasma can be explained by the evidence that the As segregation at the GaN/GaAs interface, reduces by H_2 addition. Thus, hydrogen acts to eliminate As segregation similarly to what fluorine acts in CF_4/N_2 plasma nitridation of GaAs (ref. 31). Finally, we can depict the chemical model as in the scheme shown in fig. 4 involving the following steps: nitrogen and hydrogen atoms diffusion to GaAs surface, chemical reaction at GaN/GaAs interface, and out diffusion of AsN in N_2 plasmas and of AsH in N_2/H_2 plasmas.

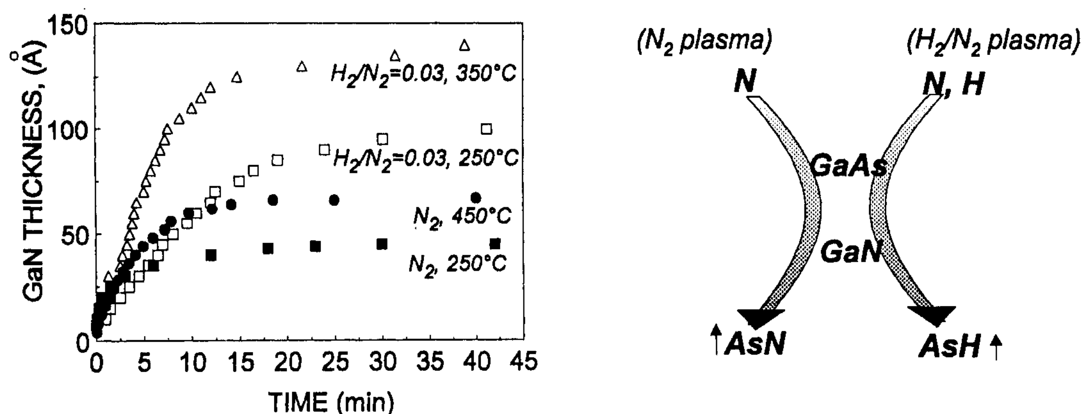

Fig. 4. GaN thickness vs. process time for GaAs nitridation in N_2 and N_2/H_2 plasmas at different surface temperatures. On the rigth, the chemical scheme discriminates the AsN and AsH desorption in, respectively, N_2 and N_2/H_2 plasmas. (N_2 plasma: 100sccm, 200 mtorr, 200 watt)

CONCLUSIONS

The present paper focuses problems of plasma-surface interaction which are frequently neglected in the interplay between science and technology.
We have shown that by developing advanced "new" surface diagnostics, such as spectroscopic ellipsometry, we can eliminate (or at least reduce) the critical gaps in experimental capabilities and we can succeed, even with the present limited knowledge of foundamental problems, in modifying and controlling surfaces submitted to plasma treatments.

In particular, from the investigation of (i) H_2 plasmas for native oxide removal, (ii) O_2 plasmas for GaAs oxidation and (iii) N_2 plasmas for GaAs nitridation, we have formulated problems on (a) the role of temperature on surface chemistry and kinetics, (b) electronic phenomena at the GaAs/oxide interface and (c) self-limiting surface kinetics. The discussion of data has provided the following answers:

- Plasma-surface interaction can be ruled by acting on surface temperature, e.g. H atoms selectively remove oxygen from InP surfaces at the optimum temperature of 230°C.
- The kinetics of the GaAs plasma oxidation is also determined by the electronic character of the surface, e.g., UV light irradiation modifies the surface electronic states and increases the oxidation rate.
- The self-limiting kinetics in GaAs nitridation is determined by the out-diffusion of As and/or AsN which limits the in-diffusion of nitrogen, e.g., favouring the As desorption by H atoms, an enhancement of the nitridation depth is achieved.

These observed phenomena are pieces of a puzzle whose uncompleted overall picture lends support to a reasonable optimism to look at the future. It is author's opinion that this mature field will be continuosly rejuvenated by new diagnostic techniques and by new experiments mainly designed to advance the knowledge of the foundamental problems.

REFERENCES

1. R.M.A. Azzam, N.M. Bashara, *Ellipsometry and Polarized Light*, Elsevier Science Publishers, North Holland (1989).
2. H.G. Tompkins, *A User's Guide to Ellipsometry*, Academic Press, Inc. New York (1993).
3. D.E. Aspnes, J. *Vac. Sci. Technol. A*, **14**(3), 960 (1996).
4. E.A. Irene, J.A. Wollam, *MRS Bulletin*, **XX**(5), 24 (1995).
5. D.A.G. Bruggemann, *Ann. Phys.* **24**, 636 (1935).
6. G. Bruno, P. Capezzuto, M. Losurdo, *Phys. Rev. B*, **54**(23), 17175 (1996).
7. M. Losurdo, G. Bruno, P. Capezzuto, *J. Vac. Sci. Technol. B*, **14**, 691 (1996).
8. H. Ninomiya, T. Sugino, K. Matsuda, J. Shirafuji, *Jpn. J. Appl. Phys.* **32**, L12 (1993).
9. E.J. Petit, F. Houzay, J.M. Moison, *J. Vac. Sci. Technol.A*, **10**, 2172 (1992).
10. L. M. Weegels, T. Saitou, H. Kanbe, *Appl. Phys. Lett.***66**(21), 2870 (1995).
11. M. Baloch, D.R. Olander, W.J. Siekhaus, *J. Vac. Sci. Technol. B*, **4**, 794 (1986).
12. N. Cabrera, N.F. Mott, *Rep. Prog. Phys.* **12**, 163 (1949).
13. R.P.H. Chang, *Thin Solid Films*, **56**, 89 (1979).
14. K. Yamasaki, T. Sugano, *J. Vac. Sci. Technol.* **17**(5), 959 (1980).
15. B.E. Deal, A.S. Grove, *J. Appl. Phys.* **36**, 3770 (1965).
16. R.P.H. Chang, A.J. Polak, D.L. Allara, C.C. Chang, *J. Vac. Sci. Technol.* **16**, 888 (1979).
17. Y.Z. Hu, Y.Q. Wang, M. Li, J. Joseph, E.A. Irene, *J. Vac. Sci. Technol. A*, **11**(4), 900 (1993).
18. P.R. Lefebvre, C. Zhao, E.A. Irene, *Thin Solid Film*, (1997) to be published
19. Z. Lu, M.T. Schmidt, D.V. Podlesnik, C.F. Yu, R.M. Osgood, *J. Chem. Phys.* **93**(11)), 795 (1990).
20. C.F. Yu, D.V. Podlesnik, M.T. Schmidt, H.H. Gilgen, R.M. Osgood, *Chem. Phys. Lett* **130**(4), 301 (1986).
21. G. Bruno, P. Capezzuto, G. Cicala, *Pure and Appl. Chem.***64**(5), 725 (1992).
22. C. F. Yu, , M.T. Schmidt, D.V. Podlesnik, E.S. Yang, R.M. Osgood, *J. Vac. Sci. Technol. A*, **6**, 754 (1988).
23. H.F. Winters, Haares, *Phys. Rev. B*, **36**(12), 6613 (1987).
24. M. Losurdo, P. Capezzuto, G. Bruno, *Phys. Rev. B*, **56**(15), 00 (1997).
25. O. Madelung, *Semiconductor: Physics of Group IV Elements and III-V Compounds*, Landolt-Bernestein, New Series, Group X, Vol. 17 (Springer-Verlag, New York, 1982).
26. S.J. Pearton, E.E. Haller, A.G. Elliot, *Appl. Phys. Lett.* **44**, 684 (1984).
27. C.Y. Hwang, M.J. Schurman, W.E. Mayo, Y.Li, Y. Lu, H. Liu, T. Salagaj. R.A. Stall, *J. Vac. Sci. Technol.A*, **13**(3),672 (1995).
28. P. Hill, D.I. Westwood, L. Haworth, J. Lu, J.E. Macdonald, *J. Vac. Sci. Technol.* B, **15**(4), 1133 (1997).
29. I.J.R. Baumvol, F.C. Stedile, J.J. Ganem, S. Rigo, I. Trimaille, *J. Electrochem. Soc.* **142**(4), 1205 (1995).
30. M. Losurdo, P. Capezzuto, G. Bruno, P.R. Lefebvre, E.A. Irene, J. Vac. Sci. Technol. xx, xx (1998).
31. S. Gourrier, A. Mircea, J.B. Theeten, M. Bacal, *Proc. 4th Int. Symp. Plasma. Chem.* Zurich, (1979).