

Ultrafine particles produced by plasma enhanced chemical vapor deposition –from SiH₄, CH₄, NH₃ and B₂H₆ gas mixtures– for nanostructured ceramics applications

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Abstract

Ultrafine particles of silicon and related binary and ternary alloys of the Si-B-C-N system produced in our research group from silane, methane, diborane, ammonia and nitrogen precursor gases by plasma enhanced chemical vapor deposition at low pressure and room temperature are reviewed. The in-situ techniques of plasma analysis and surface characterization (quadrupolar mass spectrometry, optical emission spectroscopy and ellipsometry) providing evidence of powder formation and the polymerization reactions based on the Si_nH_{2n}⁻ negative radicals electrically confined in the plasma sheath are described. The square wave modulation (SQWM) of the rf power is discussed as an efficient method of controlling the powder particle production with low particle-size dispersion. The properties of the powder particles determined by different structural characterization techniques providing their size and distribution, crystalline order and morphology, chemical composition and chemical bond vibrational characteristics, are analyzed and discussed.

Resum

Hom presenta una revisió sobre les partícules ultrafines de silici i els seus aliatges binaris i ternaris del sistema Si-B-C-N, produïdes en el nostre grup de recerca a partir dels gasos precursors silà, metà, diborà, amoníac i nitrogen, per dipòsit químic en fase vapor (CVD) reforçat per plasma, a baixa pressió i temperatura ambient. És descrita també la utilització de tècniques *in situ* d'anàlisi per plasma i de caracterització de superfícies (espectroscòpia de masses quadrupolar, espectroscòpia òptica d'emissió i el·lipsometria), que donen l'evidència de formació de partícules de pols i de reaccions de polimerització basades en radicals negatius Si_nH_{2n}⁻ confinats elèctricament en l'embolcall del plasma. La modulació d'ona quadrada (SQWM) de la font de rf és estudiada com un eficient mètode de control de la producció de partícules amb una petita dispersió de llurs dimensions. Finalment, hom analitza i discuteix les propietats de les partícules produïdes, determinades per diferents tècniques de caracterització, que permeten obtenir llurs dimensions i distribució, ordre cristal·lí i morfologia, composició química i les característiques vibracionals dels enllaços químics.

Key words: Ultrafine particles, nanostructured ceramics, silicon, silicon alloys, nanometric powder, PECVD, silicon nitride, silicon carbide, silicon carbo-nitride, boron nitride

The properties of nanocrystalline (or nanophase or nanostructured) ceramics –manufactured from ultrafine particles below 100 nm in diameter– have stimulated search for new ways to produce nanometric particles for ceramics. In this review, and as a possible alternative to the feasible methods for fabricating powders based on chemical, mechanical or thermo-physical synthesis, we will show up the plasma enhanced chemical vapor deposition –PECVD–, that is, one of the classical CVD techniques used for the manufacture of microelectronic devices, which offers new possibilities for producing high purity and monosized ultrafine particles.

In the last two decades, PECVD has been used to prepare hydrogenated amorphous silicon (a-Si:H) thin films [1-3] and dielectric layers of silicon oxides and nitrides in the fabrication of electronic and photo-electronic devices. More recently (during the last decade), hard coatings of diamond-like and amorphous carbon, BN, TiN or SiC for mechanical applications have been deposited by PECVD using appropriate gaseous mixtures of hydrides and chlorides [4-8]. PECVD allows many of these materials and other ceramic compounds to be produced in powder form.

The formation of nanometric particles during a-Si:H thin film processing with plasma techniques has been known since the early works of Spears [2]. For years, this has been considered a drawback for the growth of a-Si:H in PECVD, since powder formation was associated with a deterioration of the film quality due to the production of pinholes, roughness and porosity [9]. For that reason, fundamental research

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has been addressed to the understanding of the generation dynamics of powders and how this dynamics is influenced by the technological parameters of the discharge [10,11].

We will point out the results of our investigations on the low pressure and low temperature plasma processing technique, which has been adapted to the production of sub-micrometric (ultrafine) powder particles [12-14]. This paper focuses on the production aspects, the microstructural characterization and chemical analysis of the ultrafine powders (below 100 nm) of silicon and related compounds of the Si-C-N-B system, which were produced by PECVD using precursor gas mixtures of silane, methane, ammonia, nitrogen and diborane. The advantage of PECVD lies, on the one hand, in the possibility of producing high purity ultrafine powder and, on the other hand, that when combined with the square wave modulation (SQWM) of the radiofrequency power amplitude [15,16] it yields particles of uniform size in the range 10-100 nm through the control of the plasma-on time [17]. However, PECVD has an intrinsic limitation (less than 1g/hour yield in our experimental reactors) owing to the small amount of gas present in the reactor and the relatively low mass flow rates used. Although, this is not a disadvantage for some of the applications proposed below, for which the purity, the uniformity of size, the structural characteristics and the versatility are the most important aspects.

Ultrafine particles

Characteristics and applications

The interest in ultrafine powder particles, for ceramic and composite processing, arises from the possibility of developing tough ceramics by limiting the crack propagation [18] because of the small surface area of ultrafine particles. Furthermore, the high surface/volume ratio of ultrafine particles is associated with a high surface energy, which facilitates sinterization [19]. The relatively high specific surface (10-350 m²/g) and the chemical stability of the ultrafine particles, owing to their composition (SiC, TiN, Si₃N₄, BN), make them useful as ceramic support for catalytic applications. Other possible applications such as a smart material for photo-transducers and sensors are a consequence of the photo-emission observed in the near infrared range of the nanometric silicon powder produced by PECVD, which shows an exponential increase in the emitted power as the surrounding gas pressure decreases below 10³ Pa [20,21]. Finally, thin films of amorphous silicon have been grown by PECVD in the presence of silicon nanoparticles at low substrate temperature [22,23]. The nanostructure of these films is characterized by silicon ordered domains (1-5 nm) embedded in an amorphous silicon matrix. These silicon films exhibit thermally induced structural changes, which are associated with the recrystallization of the samples at temperatures lower than those normally used for standard hydrogenated amorphous silicon films. The recrystallization of silicon at low temperature makes new methods for the manufacture of silicon devices possible, in particular the devices

of large surface areas (solar cells, flat screens and displays).

Nanoparticles production

Ultrafine powders of silicon and their binary and ternary alloys with carbon and nitrogen can be produced by rf glow discharge decomposition of pure silane –for silicon powder– and silane/methane/ammonia (or nitrogen) gas mixtures –for silicon alloys–, and from diluted diborane and ammonia for BN powder. The processes can be carried out at room temperature, using gas flow rates in the range 20-50 sccm and gas pressures between 30 and 100 Pa. The composition of the nanoparticles depends on the relative flows of CH₄, B₂H₆, N₂, NH₃ and SiH₄, kept constant with mass flow controllers during the depletion process.

The reactor chamber [24] (Fig.1) usually consists of a cylindrical stainless steel vacuum vessel containing two parallel electrodes connected to a capacitively coupled rf power supply working at 13.56 MHz. This is equipped with a matching network that minimizes the reflected power coming from the load impedance of the discharge. The output rf power, suitable for powder production, ranges from 10 to 100 W, and the rf power amplitude can be square wave modulated (SQWM) by a function generator. This rf power range corresponds to a cathode power density from 25 to 250 mW/cm². The modulating frequencies are in the range 0.02 to 4000 Hz with duty cycles up to 50% and on-periods of at least 5 ms for the lower frequencies. In continuous wave (cw) plasma processes, the rf matching network is adapted to the load impedance by means of an automatic tuning system, but in modulated plasma processes, because the load changes during the plasma-on period, the network capacitors are locked to the tuned position of the stabilized plasma after the ignition transient.

The plasma confinement chamber is a square box that incorporates a shutter and the two parallel square electrodes with an adjustable spacing. The plasma confinement chamber geometry leads to a laminar gas flow when operated, which permits powder to be collected outside the plasma-box during the plasma-off periods. A heatable substrate-holder is placed parallel to the cathode on the ground electrode and allows films to grow in the presence of powder particles.

In order to have reproducible results it is important to control the parameters of the plasma process through, at least, the control of the pressure, the flow rate, the pumping sequence, the power and its modulation, the temperature, and the process time. The other parameters related with the optical and electrical characteristics of the plasma (the concentration of species and radicals and the *in situ* powder measurements) need more sophisticated equipment which is not strictly necessary in large-scale production of powder .

The reactor-chamber pressure was monitored by a capacitive manometer and was regulated by a pressure controller. injecting purge-gas into the mechanical pump. The overall process was controlled by a computer which can modify gas flow rate, pumping sequence, pressure, power

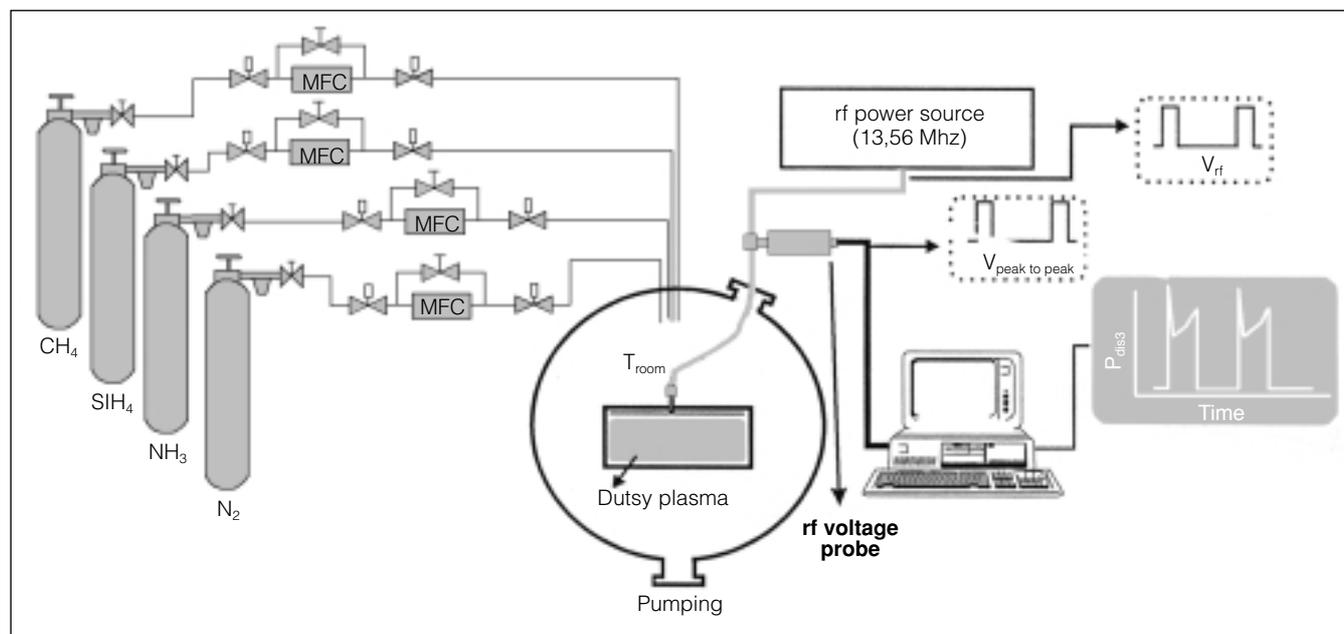


Figure 1. Schematic diagram of the plasma enhanced chemical vapor deposition equipment for ultrafine particles deposition, with details of the gas inlets, the plasma confinement chamber and the square wave modulation rf-power system.

and modulation frequency of the rf power-supply, substrate temperature and process time.

Plasma process monitoring

The reproducibility and the control of PECVD processes require the use of several plasma diagnostic techniques *in situ*. The reactor is equipped with a quadrupolar mass spectrometer (QMS), an optical-emission spectroscopy (OES) system and a phase-modulated ellipsometer (PME).

Quadrupolar Mass Spectrometry (QMS)

For the detection of species, radicals and clusters produced in a plasma process it is necessary to use the QMS at least in the range 0-300 amu. We will describe, as an example, the Hiden HAL PSM300 spectrometer, working coupled to a reactor chamber by a head placed behind the ground electrode. This arrangement allows the detection of plasma species coming from the plasma in the region close to the powder production or the growing thin film. An additional turbomolecular vacuum pump connected to the QMS cell maintains a differential of pressure through an extraction orifice usually 100 μm in diameter and 150 μm thick (conductance below 1 cm^3/s), between the reactor chamber (working-pressure in the range 10-100 Pa) and the QMS (working-pressure below 3×10^{-4} Pa). In order to determine the precursor gas whose nucleation leads to the polymerization inside the plasma, we need to measure positive and negative ions and neutral species coming from the discharge.

Optical Emission Spectroscopy (OES)

OES is used to identify species present in the plasma and to detect contamination or vacuum leaks by measuring the

wavelengths of the emitted light. The intensity of the optical emission, at a given optical wavelength, is an index of species density, the electron distribution function and the cross-section associated with the excitation of the optical level. Therefore, changes in the intensity of the optical emission are related to changes in the plasma parameters, concentration of species and electron energy. OES is used to monitor powder production in dusty plasmas because of the reduction of the intensity by light dispersion as the powder particles appear.

The OES system, described as an example for real time measurements during a plasma modulation process, consist of a diode array-based optical multichannel analyzer (OMA), Oriel Instaspec III, working in the near-ultraviolet-visible range (i.e. 300-800nm). This system analyze the plasma optical emission transmitted through a quartz window and focused to an optical fiber. The light can be resolved by a spectrograph equipped with a diffraction grating of 400 lines/mm and 1.0 nm of resolution, and using a silicon photodiode array detector composed of 1024 elements, each 25 μm wide. The output signal was transferred to a computer via a PC plug-in card. The exposure time was 20 ms and 10000 spectra were integrated in order to reduce noise effects.

Phase Modulated Ellipsometry (PME)

PME is a very sensitive optical characterization technique of the films growing in a plasma process, which can be coupled to the reactor chamber and can operate in real time mode (at fixed wavelength) or in spectroscopic mode [25] (working in a wide energy range, usually 1.5-5.2 eV). The real time mode provides the evolution of the complex reflectance ratio during the growth of the films in the presence of particles. This permits monitoring of the growth kinetics at a given wave-

length. From this evolution, the deposition rate and the film microstructure can be determined by fitting the experimental trajectories (Ψ , Δ) to theoretical growth models [15,26].

The characteristic time of the film growth in the presence of particles, when plasma is switched on and off, in the experiments of SQWM of the rf-power, is less than 10 ms. This time cannot be resolved by the conventional real-time PME, because its data acquisition rate is limited by the accuracy requirements at 25 Hz. In order to satisfy the time requirements of the SQWM experiments it is necessary to accelerate the data acquisition method of the conventional PME optical arrangement [27]. This method permits the *in situ* monitoring of the fast surface changes owing to powder deposition during the plasma-off periods. The evolution of the optical parameters of the growing film in the presence of particles can be resolved in the millisecond scale during the plasma-on and plasma-off periods, which extends the capabilities of PME arrangement and permits the analysis of fast surface phenomena.

Powder formation

Negative ions appear to have a dominant role in the formation of nanometric powder in modulated silane, methane and ammonia rf-glow discharges. Negatively-charged ions, clusters, and powder particles are confined by the plasma sheath during the plasma-on periods, which facilitates the growth of powder in particular conditions of electron bombardment and the presence of negative radicals (SiH_3^- , CH_3^- and NH_2^-). These are different from the conditions normally applied for thin film growing on the walls outside the plasma-sheath. Negative primary radicals are essentially produced in hydride discharges by primary electron attachment reactions taking place in the plasma-sheath region. The energies for dissociation are higher than 6 eV, which restricts the collisions only in the plasma-sheath region, where the electric field exists. The most probable reaction in plasma containing silane is



for electron energies of 6.7 eV. The higher energy (13 eV) required for similar methane reactions makes their existence unlikely. In addition, the production of other negative radicals, XH_2^- and XH^- , from primary electron attachment collisions is lower and also depends on less probable subsequent reactions limited by the plasma-on-time to residence-time ratio for each primary radical. This residence time depends on the probability of negative ions loss and it is clearly larger than that of positive ions because of the confinement effect of the sheath of negative potential near the electrodes. The first step in powder formation, the nucleation of particles (less than 3 nm in diameter), takes place by polymerization of the species, which needs two conditions: first, the presence of primary radicals, and second, a relatively long residence-time, which increases the

probability of collisions between radicals. These two conditions are only accomplished by the negative ions, hence neutralized ions diffuse rapidly through the plasma-sheath and deposit on the walls, and positive ions disappear from the plasma, which also contributes to the deposition. Primary negative ions can react, giving rise to a first nucleation, but additional polymerization reactions need a hydrogen loss from the surface. However, secondary negative ions (XH_n^- , $n \leq 2$) can strongly polymerize in a chain reaction, contributing to the efficient growth of the particles inside the plasma. Two technological parameters can modify the polymerization yield: rf-power and silane partial pressure, and these also affect the electron-density and the residence-time.

The fragmentation QMS spectrum (Figure 2) shows the positive ions generated from detachment reactions in a pure silane rf plasma. The Si_nH_x^+ mass peaks exhibit a deficit of the $\text{Si}_n\text{H}_{2n}^+$ species ($n = 1$ to 6), owing to the strong polymerization in a chain reaction of these radicals, which remain confined inside the plasma. The absence of positive silicon species with a number of silicon atoms above $n = 6$ indicates a blocking of the formation of large positive-charged silicon clusters due to an increase of their electron capture cross section. In contrast, big negative ions of Si_nH_x^- up to 500 uma have been detected by QMS, as reported by Howling et al. [28]. Later studies in pure silane modulated plasmas have also reported negative clusters from 28 uma to 1000 uma up to the limit of spectrometer [29].

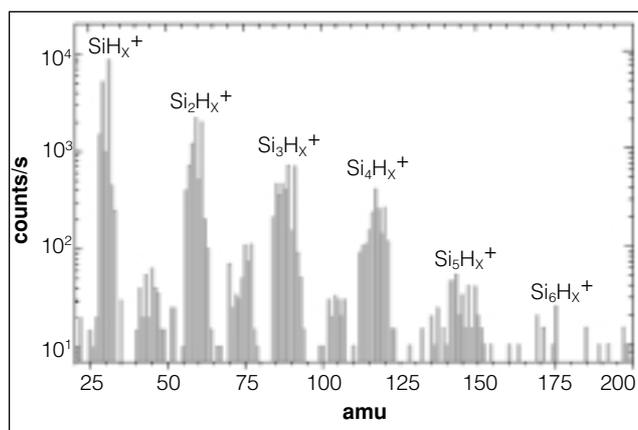


Figure 2. Fragmentation QMS spectrum of positive ions from a pure silane rf plasma. The conditions of the process were: 80 W rf power modulated by a 1000 Hz SQWM frequency at 50% duty cycle, 10 Pa total pressure, 15 sccm pure silane flow rate and room temperature.

Nanometric particles of the Si-B-C-N system

Powder needs relatively high rf-power density to form, but a rise in the energy density in the plasma chamber increases ionization and polymerization becomes more intense, which leads to uncontrolled growth of powder and to unwanted super-equilibrium hydrogen conditions. Square wave plasma modulation permits the control of the nanometric powder production through the primary parameters: plasma-on and plas-

ma-off times. Short plasma-on periods followed by long plasma-off periods favors the gas renewal with controlled gas-ratio and the expulsion of powder from the plasma-chamber.

When ultrafine particles are produced by low temperature and low pressure plasmas, it is possible to control the particles size and their composition by means of the power modulation and the precursor gas mixture, respectively. We have been able to prove that nanometric powder of Si-Si, Si-C, Si-N, Si-C-N and BN can be produced in this way, and we will now describe their more significant properties.

For applications to bulk ceramics, the main interest is to combine high melting points (2000°C) with good mechanical properties and chemical stability. Silicon carbide and boron nitride offer high mechanical strength and hardness, chemical stability in environmental conditions, and thermal shock resistance. Ternary compounds, such as SiC_xN_y and BC_xN_y may have even better properties, owing to the structural changes and packing possibilities associated with particular combinations of x and y.

Silicon powder particles

Evidence of the presence of powder and its deposition on substrates during the rf glow discharge decomposition of silane has been shown by ellipsometric measurements [30] of silicon thin films growing at different conditions of pressure and rf-power (Figure 3). Figure 3.a shows the surface changes in two rf-plasma conditions corresponding to two frequencies of square wave modulation (SQWM). Figure 3.b shows the effects of pressure on the compactness changes (related to the maximum of the imaginary part of the dielectric function $\langle \epsilon_{2max} \rangle$ determined by phase modulated ellipsometry) of amorphous silicon thin films grown in the presence of particles.

Silicon carbide ultrafine particles

a-Si_{1-x}C_x:H powder with a given x composition parameter between 0 and 1 can be produced in rf glow discharges of a

silane and methane gas mixture. The correspondence between x and the methane/silane ratio has been determined by two series of samples using different CH₄/SiH₄ ratios and keeping the other technological parameters constant: 1) Series A, with a dissipated rf-power of 48 W, modulation frequency, f_{mod} , of 100 mHz ($T_{on} = 5$ s) and a total pressure of 80 Pa. The gas ratio ($R = [CH_4]/([SiH_4] + [CH_4])$) was varied as follows: $R = 0.9, 0.75, 0.45$ and 0.1 ; and 2) Series B, at 200 mHz ($T_{on} = 2.5$ s), 48 W, 40 Pa and $R = 0.95, 0.8, 0.7, 0.6$ and 0.4 . For these series, only R has an evident effect on the structure of the powder. The color of the ultrafine powder samples of a-Si_{1-x}C_x:H changed from yellow ($R = 0.4$ to 0.6) to transparent ($R > 0.7$), depending on the silicon content of the powder. Figure 4 shows that the x factor (determined from XPS, FTIR and elemental analysis) of the a-Si_{1-x}C_x:H nanometric powder of the series B, presents a non-linear dependence on the methane fraction in the precursor gas, the silicon-carbon stoichiometry corresponding to $R = 0.8$. The elemental analysis also provides a hydrogen atomic content above 50%, which corroborates the high polymeric character of these as-deposited powder samples.

The gas composition and the rf-power supplied to the discharges has a great influence on plasma optical emission characteristics. The emission intensities of SiH (414 nm) and CH (430 nm) species, that account for the dissociative excitation of SiH₄ and CH₄ respectively, show a correlation with the [Si] and [C] contents (determined by XPS measurements) of a-Si_{1-x}C_x:H films produced by PECVD. Thus, the real time measurements of SiH and CH emission intensities can provide an easy non-intrusive method for *in situ* controlling the composition of films or ultrafine particles grown from SiH₄-CH₄ plasmas.

Silicon nitride nanopowder

Nanometric powder of Si_{1-x}N_x:H can be produced from different gas mixtures of silane, ammonia and nitrogen. Parts of our research involved a comparative study of silicon nitride

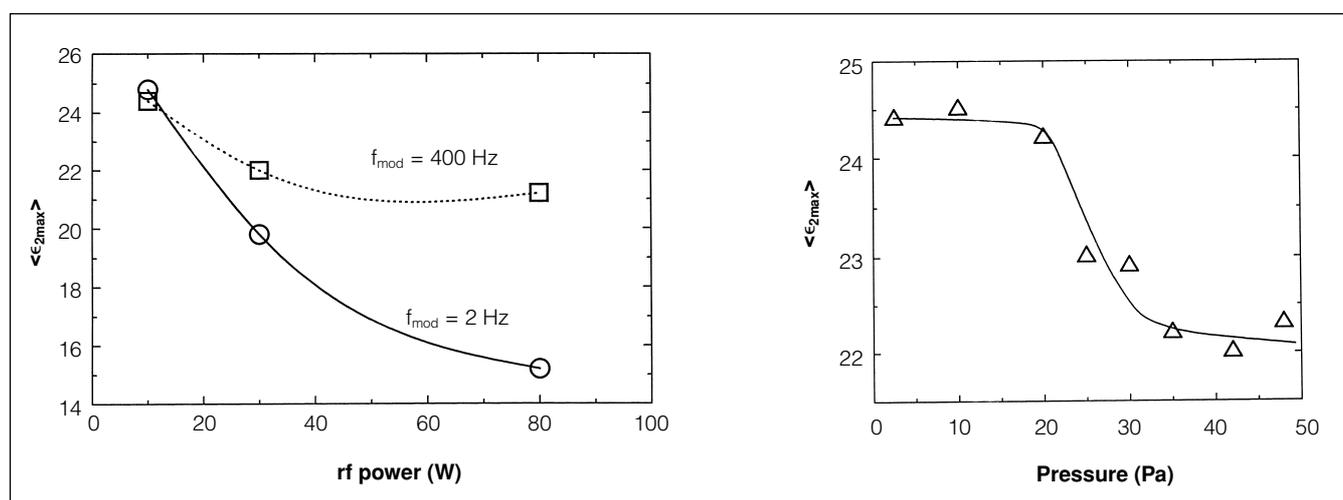


Figure 3. a) RF power effects on the maximum of the dielectric function, ϵ_{2max} , determined by ellipsometry, for a-Si:H thin films deposited from silane plasma at a substrate temperature of 300°C, at two SQWM frequencies (2 Hz and 400 Hz) and using a duty cycle of 75%. The silane flow rate and the pressure were kept at 30 sccm and at 30 Pa respectively.

b) Dependence on gas pressure of ϵ_{2max} of a-Si:H thin films deposited from silane plasma in the presence of particles. The deposition conditions were: a rf power of 20 W, a substrate temperature of 300°C and a silane flow rate of 30 sccm.

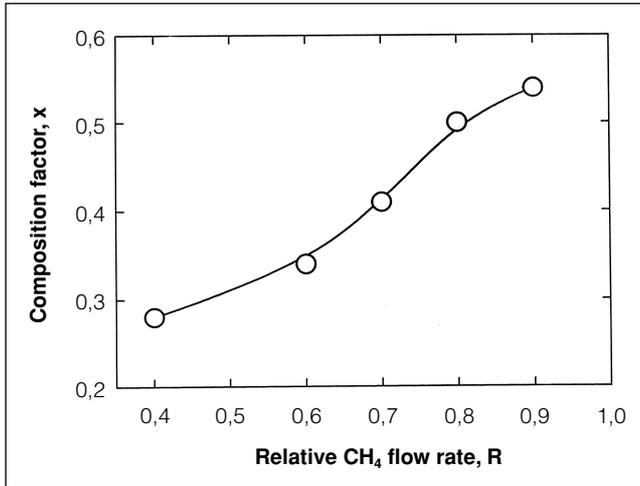


Figure 4. Composition factor, x , of the $a\text{-Si}_{1-x}\text{C}_x\text{:H}$ nanometric powder, series B, as a function of the methane fraction, $R = [\text{CH}_4]/([\text{CH}_4]+[\text{SiH}_4])$, in the rf-discharge.

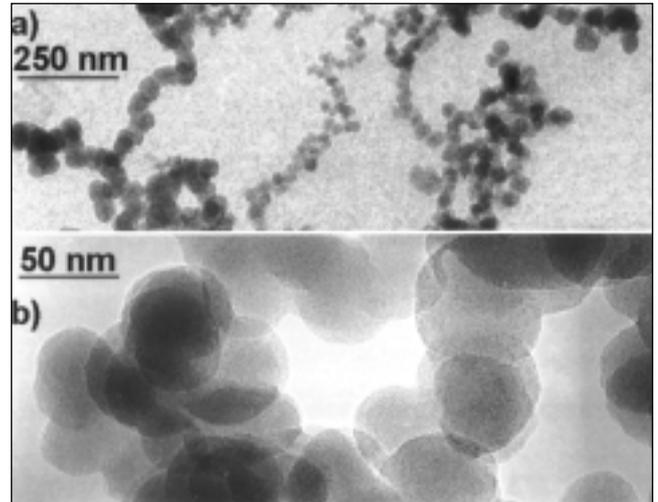


Figure 5. TEM micrographs of the SiCN powder particles produced from $\text{SiH}_4\text{-CH}_4$ mixtures diluted with a) N_2 and b) NH_3 .

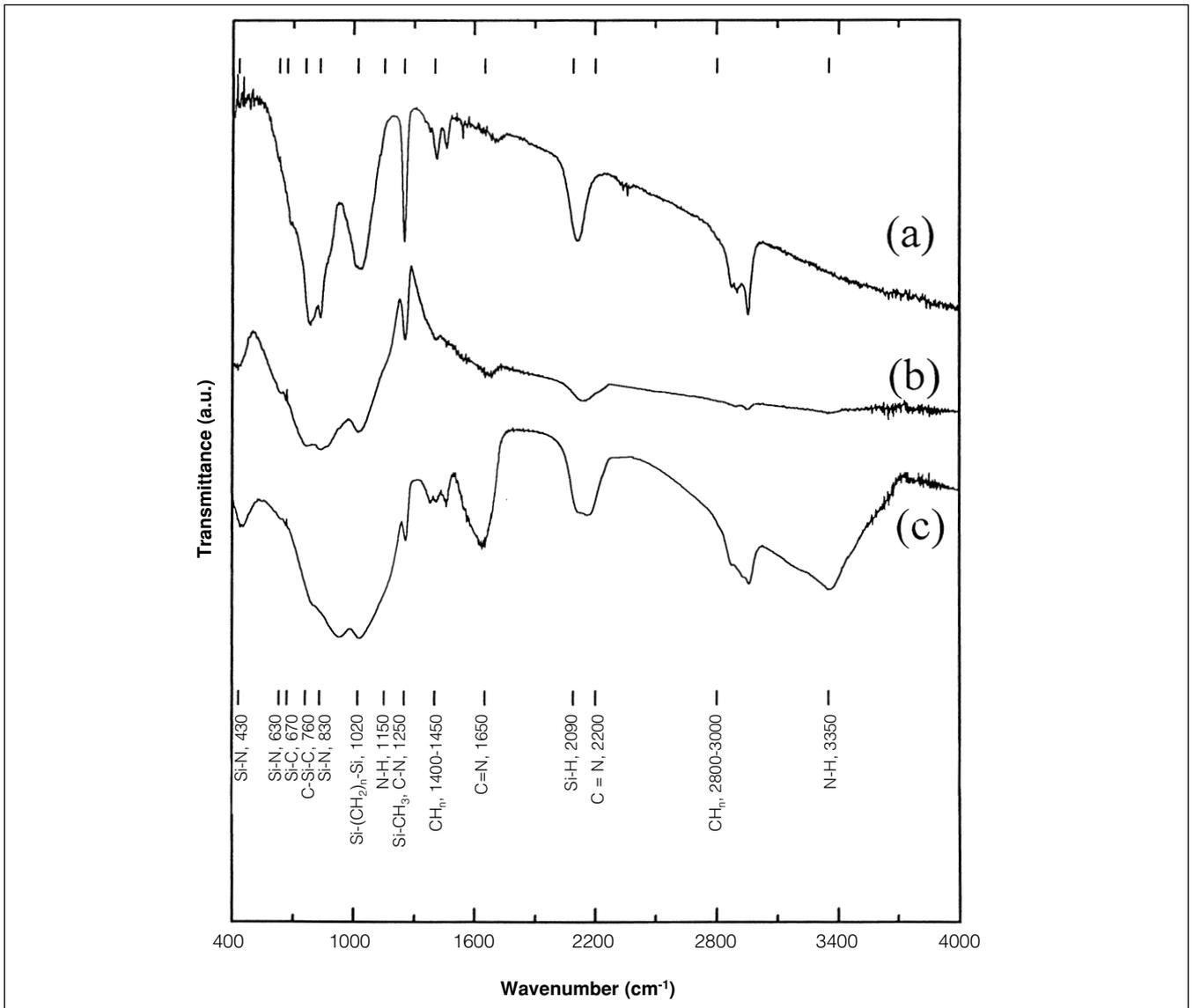


Figure 6. Infrared spectra of as-deposited $\text{SiC}_{1.3}\text{H}_{3.45}$ nanopowder (a) and $\text{SiC}_x\text{N}_y\text{:H}_2$ nanopowder produced from silane and methane mixtures with NH_3 (b) and with N_2 (c).

powder produced from two gas mixtures: 1) SiH₄ + N₂ using 5 sccm of silane and 195 sccm of nitrogen, 54 Pa of total pressure and 56 W of dissipated rf-power modulated at 333 mHz; and 2) SiH₄ + NH₃ using 24 sccm of silane and 29 sccm of ammonia, 15 Pa of pressure and 45 W of rf-power modulated at 333 mHz.

Powder from nitrogen (case 1) is slightly yellow while the powder from ammonia (case 2) is highly transparent (white). Infrared analysis provides the main differences between powder samples. In case 1, the typical absorption peaks of the Si-N bond appear at 790, 840 and 920 cm⁻¹ wavenumbers, and the hydrogen appears bonded to both silicon (630 and 2090 cm⁻¹) and nitrogen, forming N-H groups (1150 and 3350 cm⁻¹). In case 2, the Si-H bond is not present, and the Si-N bond appears as the main oscillator.

The particular chemical conditions of each case determine the observed differences. Thus N₂ is broken only at high energy while NH₃ dissociates at low energy. Hence, nitrogen is more likely to be incorporated into the powder in case 2 than in case 1. In order to increase the nitrogen content in case 1, it is necessary to introduce a high N₂/SiH₄ gas ratio along with high rf-power conditions to favor the dissociation of the N₂ molecule.

SiCN nanometric powder [17,31]

Nanometric powder of Si-C-N can be produced by SQWM rf-glow discharge from mixtures of silane-methane and N₂ or NH₃ at room temperature. As an illustrative study let us consider the main characteristics of the SiCN nanometric powder produced at f_{mod} of 200 mHz, 20% of duty cycle, and a gas flow rate of 4 sccm for silane and 13 sccm for methane. Figures 5a and 5b show TEM micrographs of the Si-C-N particles produced from N₂ and NH₃ respectively. The particles are spherical and appear to adhere forming branched structures. The diameter ranges from 25 to 45 nm. The narrow size distribution of particles could be ascribed to the short duration of plasma-on intervals, which demonstrates the efficiency of the particle-size control through the SQWM of the plasma.

The infrared vibrational analysis (Fig. 6) reveals the presence of Si-C bonds (stretching mode at 780 cm⁻¹) and different features depending on whether NH₃ (spectrum b) or N₂ (spectrum c) is used as precursor gas. The incorporation of NH₃ leads to the appearance of Si-N stretching bands at 430 and 830 cm⁻¹, along with weak absorptions related to N-H bending and stretching vibrations at 1200 and 3350 cm⁻¹, respectively. The presence of C-N bonds is shown by the small peak around 1650 cm⁻¹ (C=N) and the shoulder of the Si-H peak at 2200 cm⁻¹ (C≡N). SiCN powder obtained with N₂ gives a strong band around 900 cm⁻¹ associated with Si-N and Si-C stretching vibrations.

Boron nitride powder particles

The boron nitride nanometric powder produced by rf glow discharge of diborane and ammonia gas mixture at room temperature [32] is white and consists of agglomerated particles of diameters ranging from 20 to 100 nm. Electron diffraction patterns can be identified as the hexagonal phase

of BN, and high-resolution TEM images indicate a lattice spacing of 3.4 Å (Fig. 7) and a size of the ordered regions less than 2.5 nm. FT-IR analysis reveals that BN powder obtained by PECVD at room temperature contains hydrogen bonded in NH₂, NH and BH forms, NH₂ being the most dominant. This large hydrogenation could be due to hydrogen passivation of the particle surface or to the presence of polymeric-type BN compounds. The thermal treatment can enhance the B-N bonds while the absorption due to B-H vanishes.

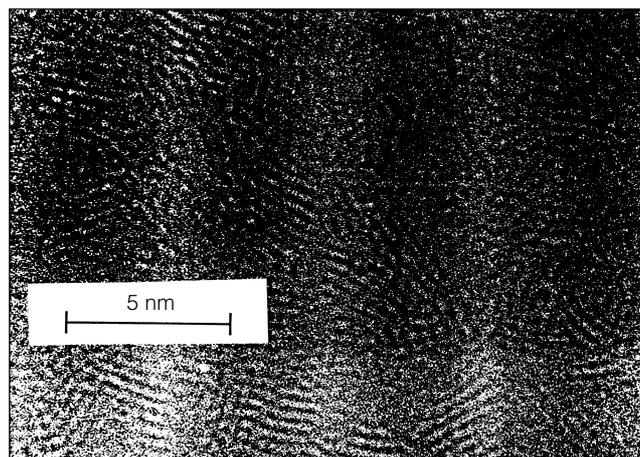


Figure 7. High resolution TEM micrograph of a BN particle. The interplanar distance is 3.4 Å.

Conclusion

In summary, ultrafine particles of silicon and related alloys of the Si-B-C-N system were produced under modulated plasma by PECVD at low pressure and room temperature, using relatively high rf-power density (up to 250 mW/cm²), from silane, methane, diborane, ammonia and nitrogen precursor gases. *In-situ* techniques of plasma analysis and surface characterization (QMS, OES and ellipsometry) were used to study the powder formation and the chemical reactions resulting in the polymerization of powder particles, based on the Si_nH_{2n}⁻ negative radicals electrically confined in the plasma sheath. The SQWM of rf power has proven to be an efficient method of controlling the particle size with low dispersion. The properties of the ultrafine particles were determined by several structural characterization techniques, which gave their size and morphology, crystalline order, chemical analysis and vibrational properties.

Acknowledgments

This review is based on experiments carried out in the Grup de Física i Enginyeria de Materials Amorfs i Nanoestructures since 1991. During this period, we have collaborated in two projects of the BRITE EURAM program and we would like to acknowledge the contribution to our experience of our partners Dr. J. Perrin, Dr. G. Kroesen, Dr. Ch. Hollenstein, Prof. A. Bouchoule, Dr. P. Roca i Cabarrocas, Dr. J. C. Bertolini

and all the other colleagues present in the multiple workshops and discussions on powder particles. We also express our acknowledgement to Prof. P. Roura for useful discussions. The authors thank the Serveis Científico-Tècnics of the University of Barcelona for the structural and analytical measurements. At the present time our research activity is supported by the CICYT, Madrid, under contracts MAT94-1511-CE and MAT96-1194-C02-01.

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About the authors

The group of Physics and Engineering of Amorphous Materials and Nanostructures (FEMAN) from the Department of Applied Physics and Optics of the Barcelona University focusses the activity on the study of the amorphous materials and nanostructures. The main objectives are the production of compounds of the B-C-Si-N-H system as thin film and as nanometric powder, the structural and compositional characterization and the determination of the physical properties. The group uses several techniques based on process in reactive atmosphere at low pressure by means of chemical vapour deposition (CVD) activated by plasma, and physical vapour deposition (PVD) such as rf magnetron sputtering, sputtering assisted by ion beam and electron beam evaporation.

The characterization of materials carried out by the group consists on the determination of the micro and nanostructural

properties, composition and physical properties by diverse techniques of chemical analysis and crystallography, electronic microscopy and several techniques of vibrational, optical, electrical and mechanical characterization. The activity of the group has been focussed on the binary and ternary compounds: Si:H, C:H, SiN, SiC, SiCN, BC, BCN, which show singular properties concerning their mechanic characteristics, such as, hardness, friction and wear. The group is interested in the nanostructured materials obtained from CVD processes, which show a high hydrogen content and an extreme porousness associated to the nanometric size of the particles of powder. The interest for the thin film materials studied by the group is a consequence of their applications in the processes of synterization of ceramic materials and cermets, manufacture of ultrafiltration membranes, ionic storage and ion conductors.
