CONF-9510236--1

SAND95-2359C

Synthesis of Silicon Nitride Particles in Pulsed Rf Plasmas

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ABSTRACT

Silicon nitride (hydrogenated) particles are synthesized using a pulsed 13.56 Mhz glow discharge. The plasma is modulated with a square-wave on/off cycle of varying period to study the growth kinetics. *In situ* laser light scattering and *ex situ* particle analysis are used to study the nucleation and growth. For SiH_4/Ar and SiH_4/NH_3 plasmas, an initial very rapid growth phase is followed by slower growth, approaching the rate of thin film deposition on adjacent flat surfaces. The average particle size can be controlled in the 10-100 nm range by adjusting the plasma-on time. The size dispersion of the particles is large and is consistent with a process of continuous nucleation during the plasma-on period. The large polydispersity is also reported for silicon particles from silane and differs from that reported in other laboratories. The silicon nitride particle morphology is compared to that of silicon and silicon carbide particles generated by the same technique. Whereas Si particles appear as rough clusters of smaller subunits, the SiC particles are smooth spheres, and the Si_3N_4 particles are smooth but non-spherical. Post-plasma oxidation kinetics of the particles are studied with FTIR and are consistent with a hydrolysis mechanism proposed in earlier work with continuous plasmas. Heat treatment of the powder in an ammonia atmosphere results in the elimination of hydrogen, rendering the silicon nitride resistant to atmospheric oxidation.

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INTRODUCTION

There is great interest in obtaining ceramic particles in the ten nanometer size range in order to fabricate ceramic objects with improved properties. It has been long recognized that silicon nitride has excellent high temperature structural properties such as high strength and low weight which would make it ideal for many applications such as engine parts. Unfortunately, the low temperature properties of hardness and brittleness make manufacturing processes difficult. It is known that materials formed from nanometer size subunits can exhibit improved macroscopic properties such as enhanced ductility or superplasticity. Also, in order to obtain the optimum properties, it is important to achieve microstructural and chemical homogeneity with minimal defects in a nearly fully dense ceramic. This is facilitated by starting with fine-particle-size powders that have low impurity content.

Obtaining the ultrafine powders that are needed for exploratory research as well as manufacture has proven to be a problem. A variety of techniques are currently used to produce commercial silicon nitride powders[1]. These include direct nitridation of silicon, carbothermic reduction of silica and gas-phase reaction of $SiCl_4$ and NH_3. Several other gas-phase processes have been reported including the thermal pyrolysis of silane and ammonia[2] and laser pyrolysis of gaseous reactants[3]. Each of these processes has limitations in the morphology, size distribution, and chemical purity of the product.

In 1988, Ho et al[4] used an rf glow discharge to synthesize large quantities of nanosize silicon nitride particles and other materials in a radio frequency (rf) plasma. Properties of the powder were well characterized by a variety of techniques. One particular limitation of the technique is a lack of control of particle morphology and size. The continuous SiH_4/NH_3 plasma yields a distribution of particle sizes, averaging 100-200 nm diameter and includes significant agglomeration.

In 1992, Boufendi and coworkers[5] reported studies of the formation of silicon particles in a silane/argon plasma by pulsing the plasma on for a short time and collecting the particles for electron microscopy. Remarkably, they found a linear rate of particle growth to the 40 nm size with a very narrow size dispersion. They postulated an initial stage of the plasma in which nucleation occurs, producing a high density of 5 nm size particles followed by a no-nucleation stage in which these smaller particles associated into the observed clusters. Many more studies have been reported on the generation of silicon particles in silane plasmas making this arguably the best understood plasma-particle system[6].

We report here experiments aimed at applying a pulsed plasma approach to the synthesis of nanosize silicon nitride powders. The technique is tested using silane/argon for comparison with the earlier work Some striking differences in particle growth rates and size dispersion are reported. Applying the pulsed plasma technique to the silicon nitride system, we demonstrate control of the average particle size but observe persistent size dispersion and agglomeration.

EXPERIMENTAL

Experiments are performed in a cubic aluminum chamber, 46 cm. length, mechanically pumped to the 1 mTorr base pressure range. A diagram of the electrode assembly and powder collection is shown in Figure 1. The plasma assembly consists of a 15 cm. diameter powered electrode, perforated with holes to allow gas flow in a showerhead configuration. The plasma region is enclosed on the sides by a grounded aluminum sheet with a grounded high transmission screen across the bottom. The distance from the powered electrode to the confining screen is 3 cm. The 15 cm. diameter pumping port is located beneath the electrode assembly (4-15 cm. distance), and is fitted with a single sheet of Whatman #1 filter paper. Transmission electron microscopy (TEM) is employed *ex situ* in order to study the size and morphology of the particles generated. To obtain samples, a TEM sample grid is placed beneath the plasma assembly on the filter paper.

A 10 mWatt helium-neon laser passes through the region beneath the plasma (or through holes in the electrode assembly wall). Laser light scattering from particles is observed by eye as a qualitative characterization of the process.

Amorphous hydrogenated silicon particles are generated from silane/argon gas mixtures, typically, 1-2 sccm silane, 30 sccm argon, 200 mTorr pressure. Hydrogenated silicon nitride particles are produced in a silane/ammonia discharge, typically 10 sccm SiH_4, 60 sccm NH_3, 500 mTorr pressure. For morphology comparison, some silicon carbide particles are synthesized from a methyltrichlorosilane/hydrogen plasma with a flow rate ratio of 1:10 and a pressure of 350 mTorr.

In a typical experiment, gas flow is first established; then, the plasma is pulsed with a square wave on/off cycle for 100 periods. The TEM grid is then removed and analyzed. In order to obtain large quantities of powder for bulk analysis, the plasma is pulsed for several hours and the filter with accumulated powder is removed.

Experiments are conducted to verify that the flow is laminar. Flowing 10 sccm SiH_4 and 60 sccm NH_3, at 500 mTorr pressure, a continuous plasma is operated for 10 minutes. Black construction paper replaces the filter paper covering the 15 cm. diameter pump port and the pattern of white powder accumulated on the paper is readily visible.

RESULTS AND DISCUSSION

Silicon

In a study aimed at duplicating the experimental conditions of Boufendi et al[5], we investigated the formation of silicon particles in a silane/argon plasma. Using conditions similar to those of Ref. 5, (flowing 2 sccm SiH_4, 28 sccm Ar, at 200 mTorr pressure, 560 Volt rms) we generate amorphous hydrogenated silicon particles. We find that the growth kinetics differ very markedly from those of the previous study. In Fig. 2 is shown the measured size distribution for silicon particles as a function of plasma-on time with the upper and lower solid line giving one standard deviation. Shown for comparison are dashed lines depicting the distribution obtained under apparently similar conditions by Boufendi et al. We observe an initial rapid growth in particle diameter (70 nm/sec) which, for longer plasma on-periods, decreases to a slow growth rate (0.5 nm/sec) comparable to growth rate on the walls. Growth rate of deposited film on substrates placed on the screen is measured to be 0.3 nm/sec. In addition, the size dispersion is very large, in fact, with all sizes from zero to approximately twice the average diameter about equally represented.

We are unable at this time to resolve the discrepancy between our particle growth dynamics and those of Boufendi et al. We verified that the plasma off-time (from 1-10 secs., typically 2 seconds) played no role; the linear flow rate of gas under our conditions is 10 cm/sec, so that the particles should be swept from the plasma region in less than a second. The flow was demonstrated to be laminar by operating a continuous plasma of silane/ammonia and observing the pattern formed on black construction paper placed over the exit port 15 cm from the plasma-confining screen. The image of the screen was very well reproduced on the paper. It might seem surprising that the particles which are charged negative with respect to the plasma can surmount the potential barrier to pass through the screen. The particle experiences a combination of forces including fluid drag, ion drag, gravitational and, possibly, a thermophoretic force directed against the electrostatic barrier to passing the screen. The fluid drag, ion drag, thermophoretic force and particle charge all scale as the particle radius squared. Thus, particle growth should not greatly affect the force balance unless the particle mass became great enough that gravity begins playing a role. It seems more likely that the screen hole size, 1.4 mm, is large enough that there is a significantly lower barrier for a particle to pass through the center of the hole than near the wires themselves. Perhaps this electrostatic barrier is sufficiently reduced that the combination of forces is adequate to push the particle across.

No variation of pressure, flow, rf power, or gas mixture reduced the agglomeration or size dispersion noticeably. Although much effort was expended to match conditions of geometry, linear flow velocities, pressure and power, we were unable to observe the nearly monodisperse, unagglomerated silicon particle growth observed by Boufendi et al. Plasmas are, however, notoriously difficult to reproduce quantitatively in different laboratories. We are not actually able to confirm, at this time, that the plasma density, spatial uniformity, or temperature coincide with those of Boufendi et al.

The silicon particles (Figure 3A) exhibit a structured surface morphology, with a roughness on the 5 nm scale, very similar to that reported by Boufendi et al. This surface texture may result from a growth mechanism which consists of the agglomeration of 5 nm diameter particles as has been suggested. Alternatively, a molecular growth mechanism involving island formation on the surfaces may lead to rough surface topography, including in the chemical vapor deposition of silicon[7]. It is also possible that the sub-structure of these particles is more elaborate than is apparent with our TEM resolution. The particles may even have a fractal type morphology as has been seen for other plasma-generated particles by Garscadden, Haaland, Ganguly and Williams[8,9].

Silicon Nitride

Particles are readily formed in a pulsed rf discharge of silane/ammonia gas mixtures. The chemistry of the particles appears consistent with our earlier observations using a continuous rf plasma[4]. Fourier transform infrared spectra (FTIR) (Figure 4) show strong SiH (2130 cm^{-1}) and NH absorptions (3360 cm^{-1} and 1550 cm^{-1}), confirming that the powder has a high hydrogen content. In the earlier work, the stoichiometry of the particles was found to depend on the silane to ammonia ratio in the inlet gases, and the color of the powder was indicative of the stoichiometry, varying from dark brown (pure silicon hydride) to white (SiN_2H_2). The powders formed in a pulsed plasma with 6:1 ratio NH_3/SiH_4 are white corresponding to a stoichiometric ratio of Si/N, but elemental analysis has not yet been performed on these powders.

Fig 3B. is a TEM picture of silicon nitride particles formed with 100 cycles of a 0.2 sec-on discharge. The average particle size determined from analysis of many TEM photos is 15 nm diameter. It is clear that many particles have agglomerated into clusters or chains and that the size dispersion is large. Similar pictures were analyzed for different plasma on-times and a sample of the results is shown in Fig. 5. The average diameter is shown with a solid dot and is seen to increase fairly linearly in time. The average particle grows at a rate (72 nm/sec) comparable to the growth rate of silicon particles in the silane/argon plasma. At longer times, not shown, the rate of growth slows similar to the behavior of silicon shown in Fig 2. In Fig. 5, a point has been graphed for each measured particle to show the distribution of sizes. Clusters and agglomerates are not included. It appears that particle nucleation is an ongoing phenomenon during the plasma-on period. All sizes of particles are approximately equally represented and the simplest model is that a particle may nucleate at any time and it then grows at a constant rate until the plasma is extinguished. The particles do not exhibit the rough surface morphology seen in the silicon particles. For all sizes from 5 nm to 200 nm diameter, the particles appear smooth with our TEM resolution. The particles are generally not spherical but have oblong or lumpy outlines which suggest agglomeration with continued growth of an overlayer. Initial experiments aimed at synthesizing silicon carbide from methyltrichlorosilane/hydrogen mixtures result in particles which are polydisperse, smooth and quite spherical, resembling the fluorocarbon particles previously reported[10]. It is clear that the mechanisms of particle growth differ for each of the chemistries and much work remains to sort out the connection between chemistry and morphology.

The observed agglomeration of particles is potentially detrimental to the goal of producing high density ceramic material. It is generally expected that hard agglomeration into complex shapes will seriously degrade the ability to obtain close packing. It is important to establish the physical mechanisms leading to agglomeration. An isolated body suspended in a plasma acquires a negative potential relative to the plasma. We would expect that the negatively charged particles should repel each other and remain separated. For very small particles, the charge will be sufficiently small that random fluctuations will lead to occasional neutralization. There is much evidence in our TEM photos for agglomeration occurring at all sizes of particles, including 100 nm diameter where charge accumulation should be too large (hundreds of charges) to allow random neutralization. When the plasma is extinguished, though, the particles may be neutralized by the residual ions and could agglomerate through collisions.

Close inspection of the agglomerates seen in TEM photographs reveals that some are very strongly fused as if significant material growth has occurred after association of the particles. This would seem to point to a mechanism of agglomeration in the plasma itself at least for some particles. The smooth appearance of the particle surface might suggest melting and neck-formation by mass transport. The temperature of the gas and ions in the plasma is, however, very low, probably less than 50 C. The particle is presumably nucleating and growing by highly exothermic reaction of radicals which might heat the growing particle faster than it can radiate. If the particle were to exceed 1000 C (still well below the melting point), however, it would desorb the bound hydrogen, in conflict with the post-plasma FTIR results. Thus, particle melting should be discounted.

When laser light scattering is monitored either in the bulk of the plasma, or beneath the electrode assembly (with and without the lower screen), no particles are observed during the on-cycle. A sudden appearance of light scattering occurs only in the instant after the plasma is extinguished. The individual particles below 100 nm do not scatter enough laser light to be visible by this technique, thus it appears that a burst of agglomeration occurs after the plasma is turned off.

Silicon nitride particles generated by the pulsed plasma technique are found to be very air sensitive. When a freshly synthesized sample is placed in the FTIR and monitored hourly, the SiH bonds are seen to decrease while the SiO bonds increase. In Figure 4B is seen the difference spectrum for powder exposed to ambient air for 48 min. The oxide absorption at 1075 cm $^{-1}$ has grown while the NH (1550 and 3360 cm^{-1}) and SiH (2130 cm^{-1}) absorptions have been altered. The SiH_n peak appears to have shifted as if some SiH groups (~2070 cm^{-1}) have been preferentially removed with growth of other SiH_n functionalities (2230 cm^{-1}). It is difficult to assign these absorptions as is possible with amorphous silicon[11], because the presence of nitrogen and oxygen will alter the bonding characteristics of the SiH functionalities. The time constant for growth of the oxide is strongly dependent on humidity. The powder synthesized by the pulsed plasma technique (mean diameter 15 nm) was found to oxidize significantly faster (greater than a factor of 2) than the powder from a continuous plasma (mean diameter 150 nm). This is presumably because the rate is dependent on the surface area to volume ratio which is an order of magnitude larger for the small particles.

For purposes of powder handling in studying the sintering properties, the air sensitivity is inconvenient. Experiments were conducted to explore the chemistry of the particles under post-plasma heat treatment. When the 15 nm diameter powder is heated in vacuum to 800 C for one hour, it changes color from white to dark brown, and the hydrogen and nitrogen functionalities are lost from the FTIR spectrum. This is different behavior from that of the larger particles from the continuous plasma which were found to retain most of the nitrogen. It is possible that a diffusion barrier prevents nitrogen loss from the bulk of the large particles. Heat treatment of the pulsed plasma Si_3N_4 particles at 800 C in an ammonia atmosphere (200 Torr) for 20 minutes results in the loss of the air sensitive SiH functionality as seen in Figure 6A. Some NH functionality remains. The powder is found to be relatively insensitive to air as is seen in Figure 6B, the difference spectrum for a heat-treated sample exposed to air for 24 hours. No evidence for SiO growth is observed.

CONCLUSIONS

The pulsed rf plasma technique using silane/ammonia gas mixtures is capable of generating silicon nitride particles in the ten nanometer size range. Large size dispersion and much agglomeration are always observed. Similar agglomeration is observed for silicon particles grown from silane/argon mixtures. The distribution of particle sizes for initial growth to approximately 80 nm suggests a mechanism of continuous nucleation with linear radial growth. Some agglomerates appear to be formed by association in the plasma while laser light scattering shows a burst of agglomeration immediately after the plasma is extinguished. Plasma generated silicon nitride particles are sensitive to hydrolysis by water vapor in air but can be stabilized by post-plasma heat treatment in ammonia. The kinetics of oxidation and thermal loss of hydrogen/nitrogen show strong particle size differences.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the assistance of Dr. Pauline Ho for valuable discussions and of Charles Hills for obtaining the TEMs. Also, this work was supported by the United States Department of Energy under Contract DE-AC04-94AL85000.

DISCLAIMER

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FIGURE CAPTIONS

1. Schematic of the pulsed plasma apparatus.

2. The size distribution of silicon particles from a pulsed rf discharge vs. plasma on-time. Solid lines are one standard deviation. Dashed lines are approximately the results for similar conditions from Ref 5.

3. TEM photograph of particles generated in the pulsed plasma. A) Silicon 0.5 sec silane/argon plasma, B) Silicon nitride, 0.2 sec silane/ammonia plasma.

4. FTIR spectra of silicon nitride particles, 0.2 sec silane/ammonia plasma. A) Fresh powder from plasma. B) Difference spectrum of powder after 48 min exposure to ambient air.

5. Silicon nitride particle size distribution for different plasma on-times. Large dot is the average diameter. Small dots are individual measurements.

6. FTIR spectra of heat-treated silicon nitride particles, 0.2 sec silane/ammonia plasma, 800 C, 20 min., ammonia atmosphere. A) Freshly heat-treated powder. B) Difference spectrum of powder after 24 hour exposure to ambient air.

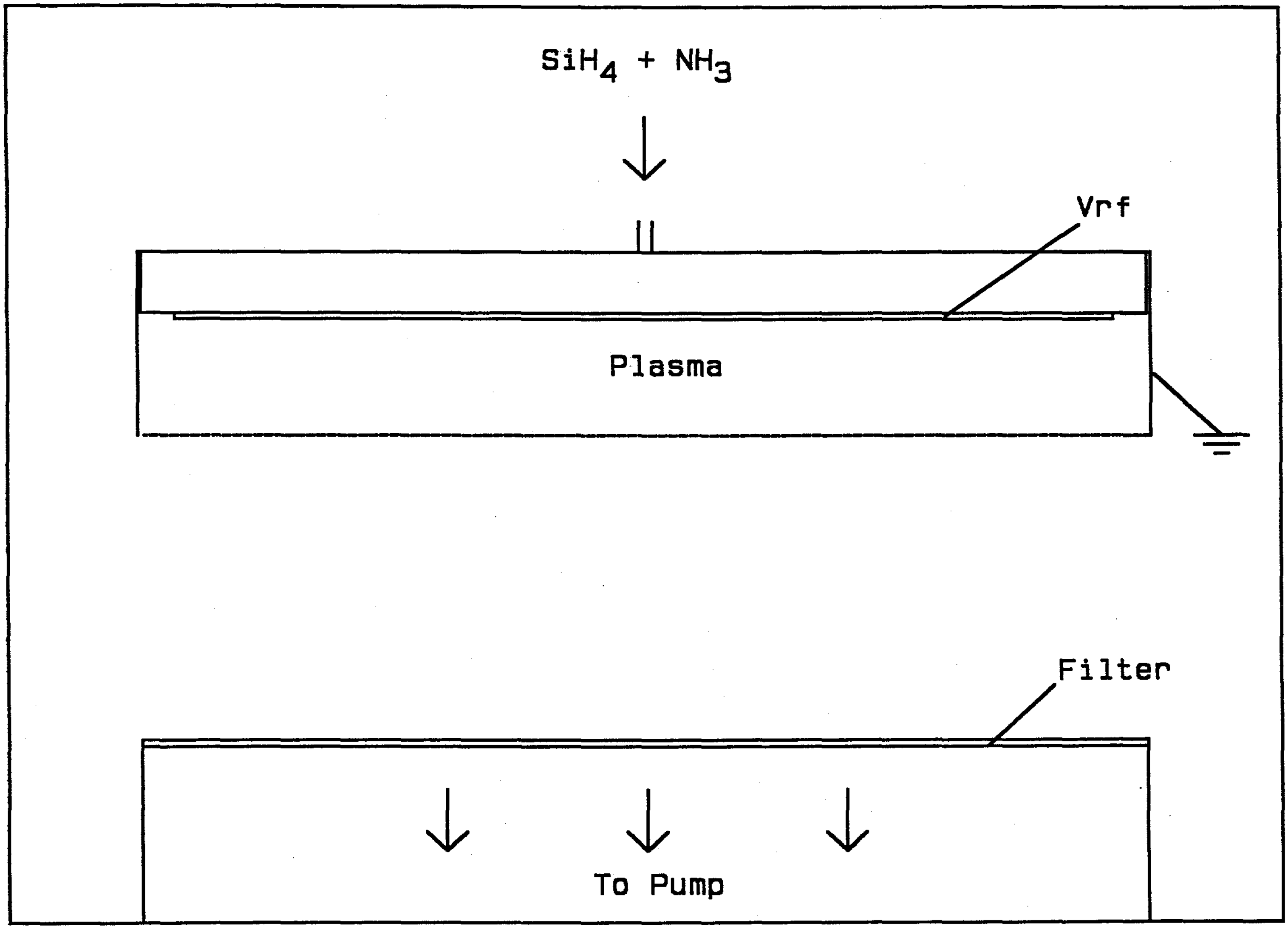
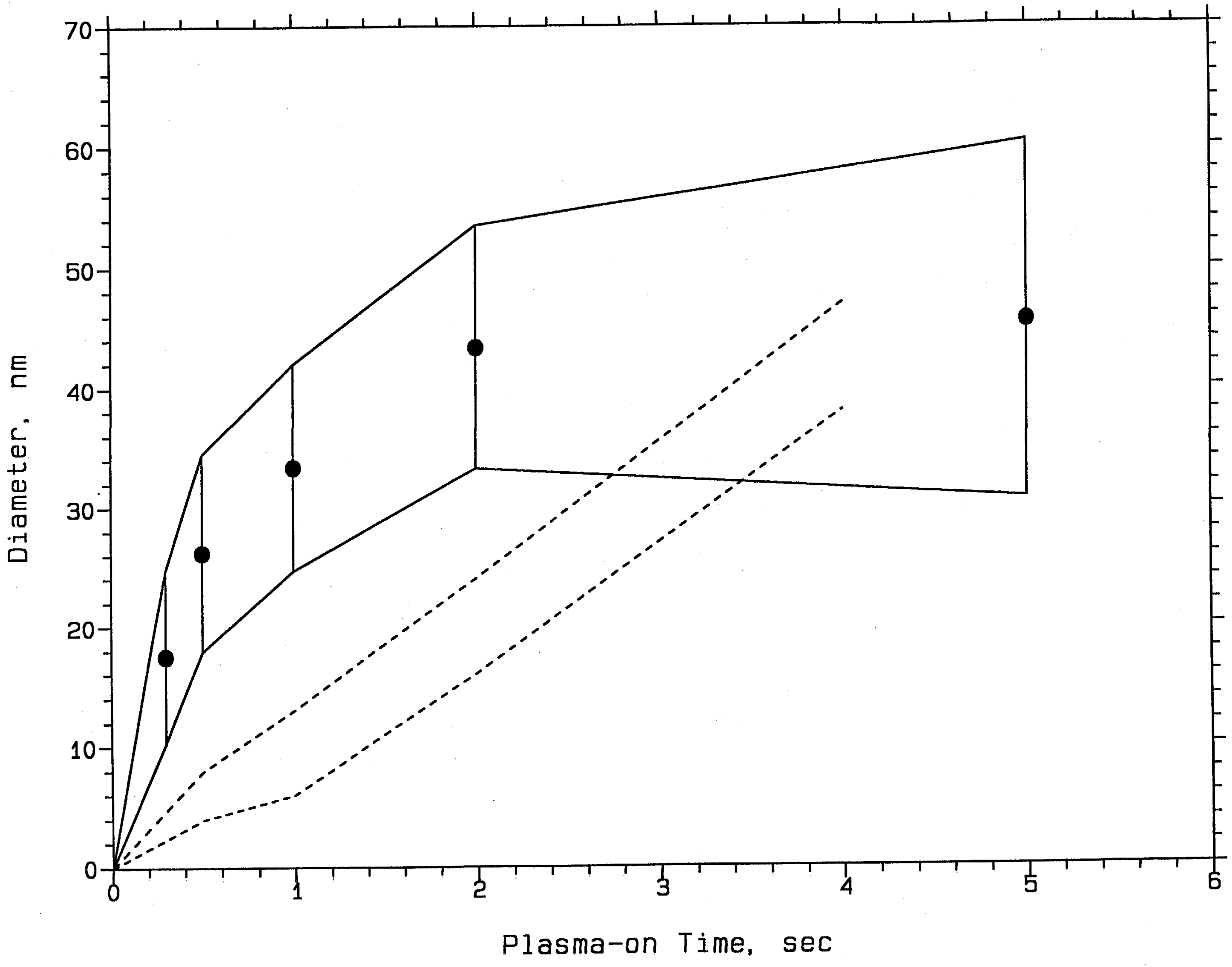
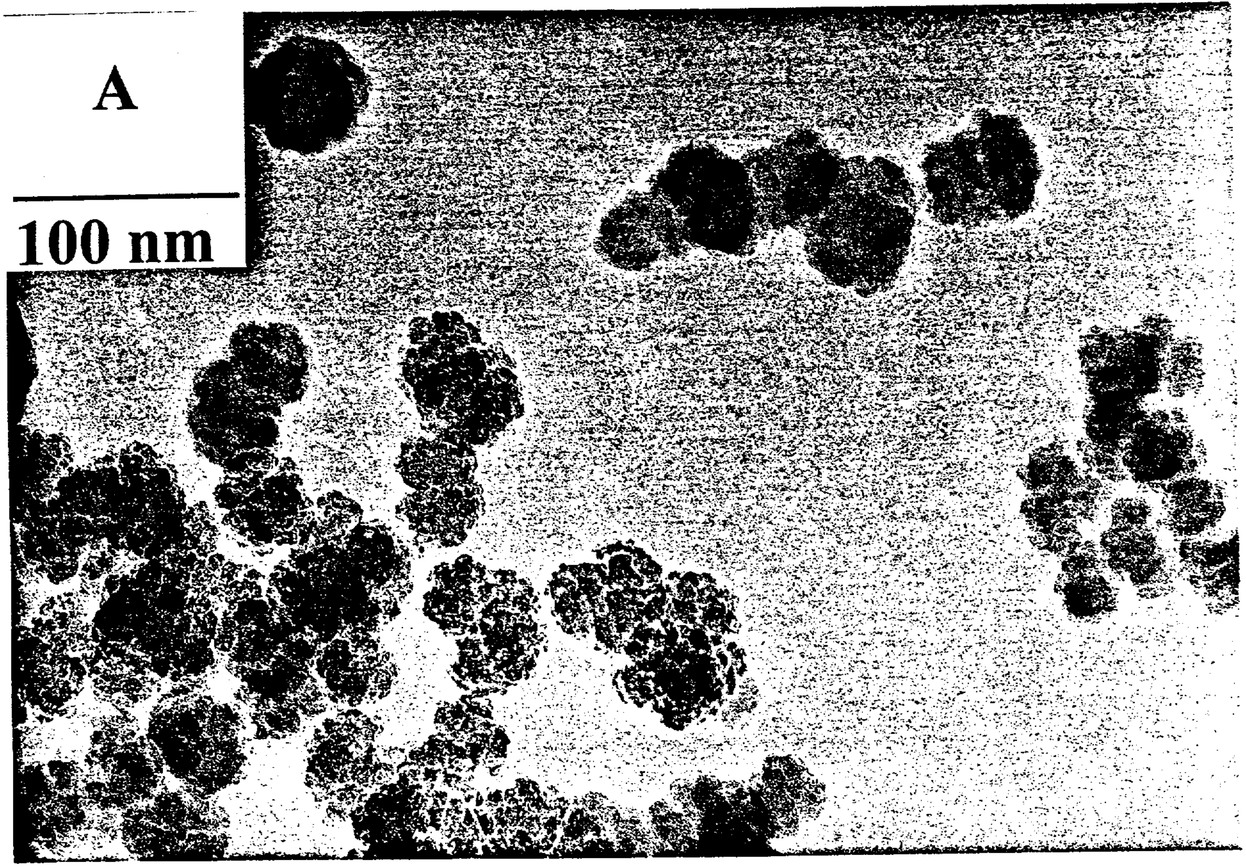


Fig 1


70
60
50
40
30
20
10
0
Diameter, nm
0
1
2
3
4
5
6
Plasma-on Time, sec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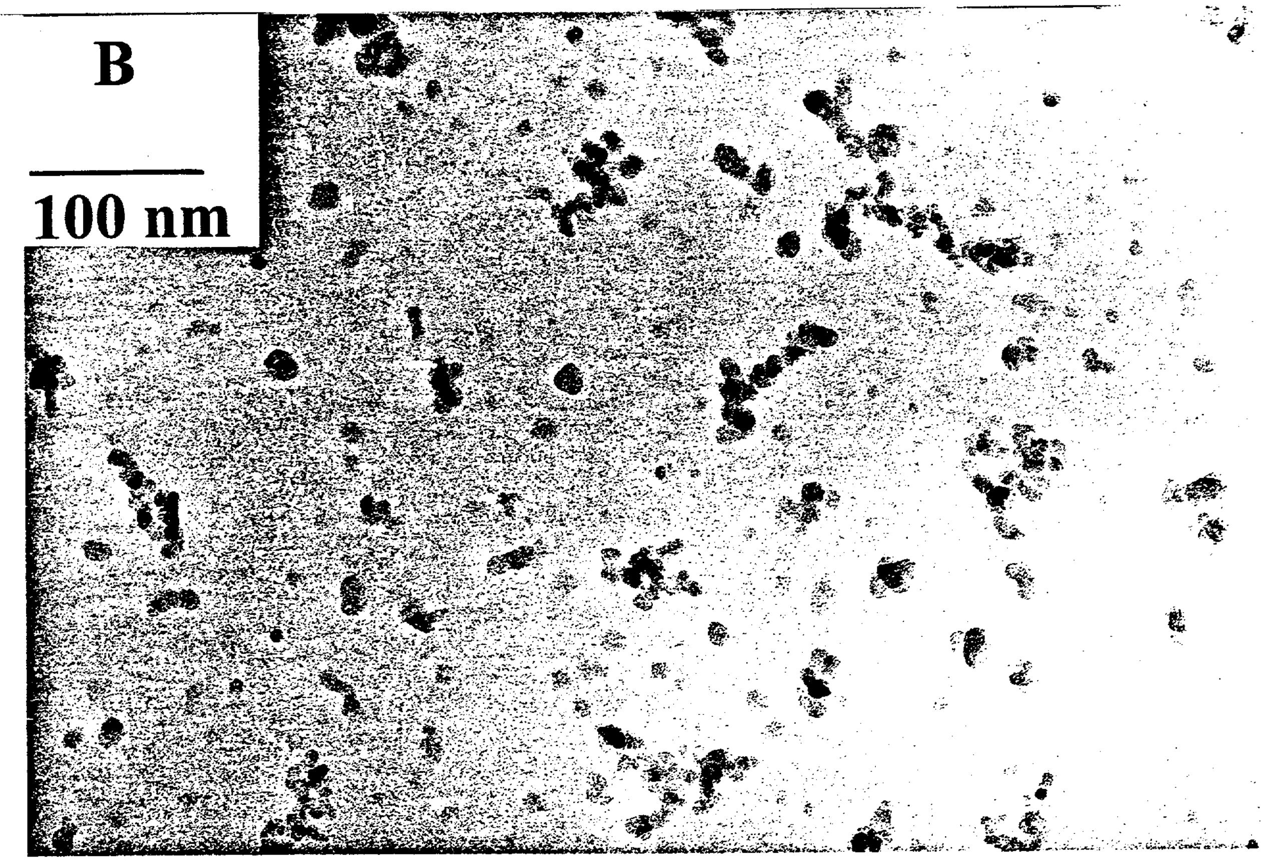
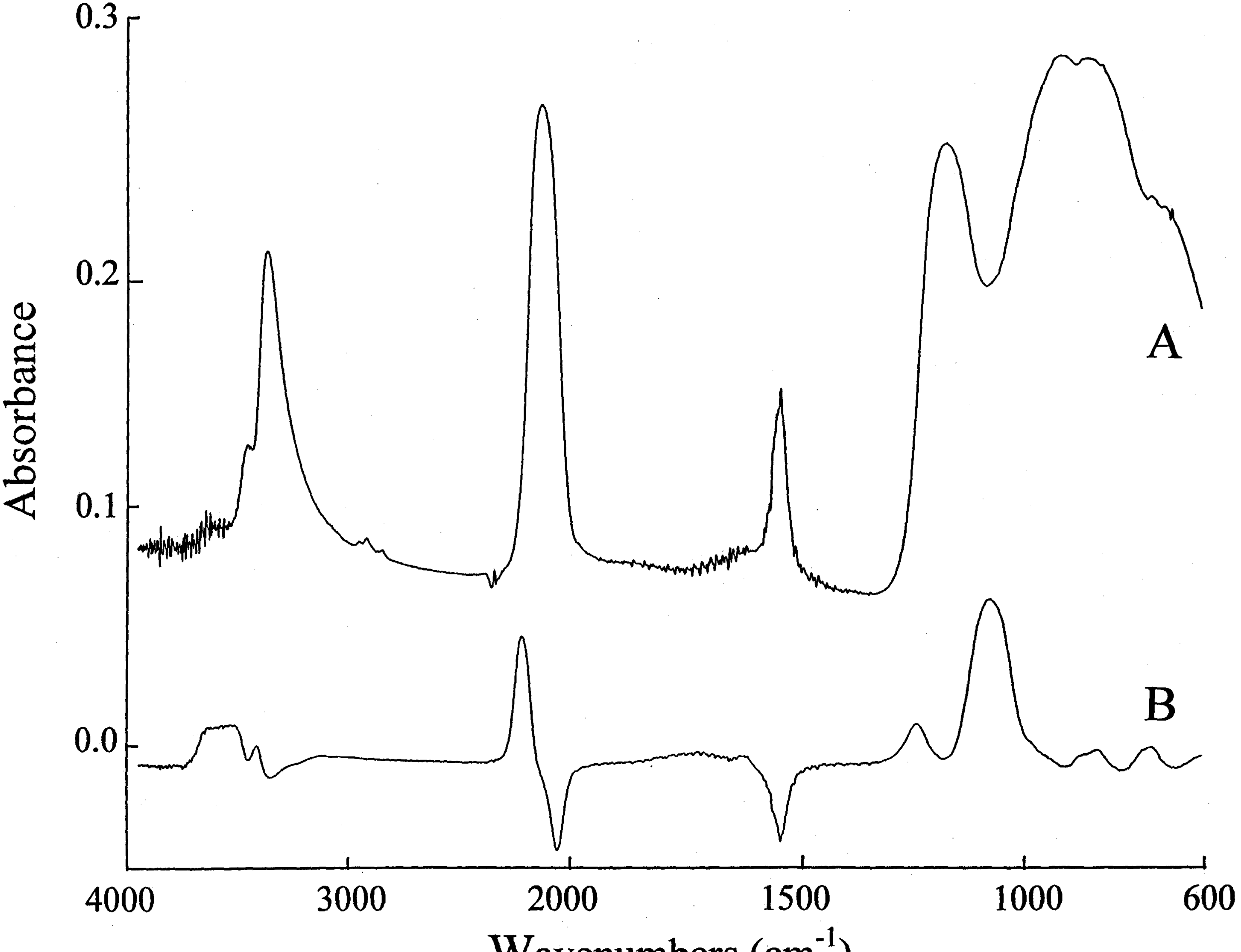
100 nm


B
100 nm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0.1
0.0
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A
B
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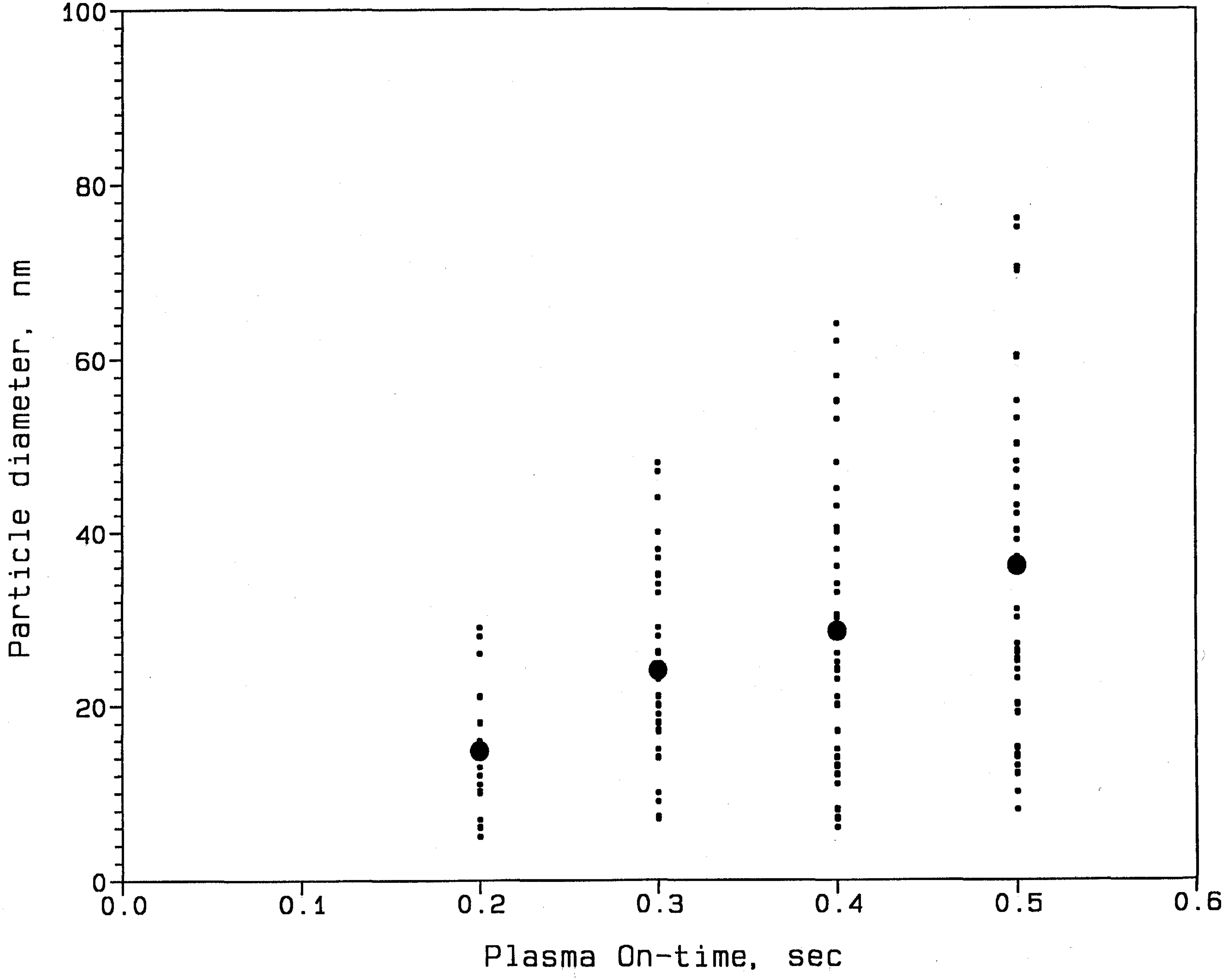
3000
2000
1500
1000
600
Wavenumbers (cm^{-1})


100
80
60
40
20
0
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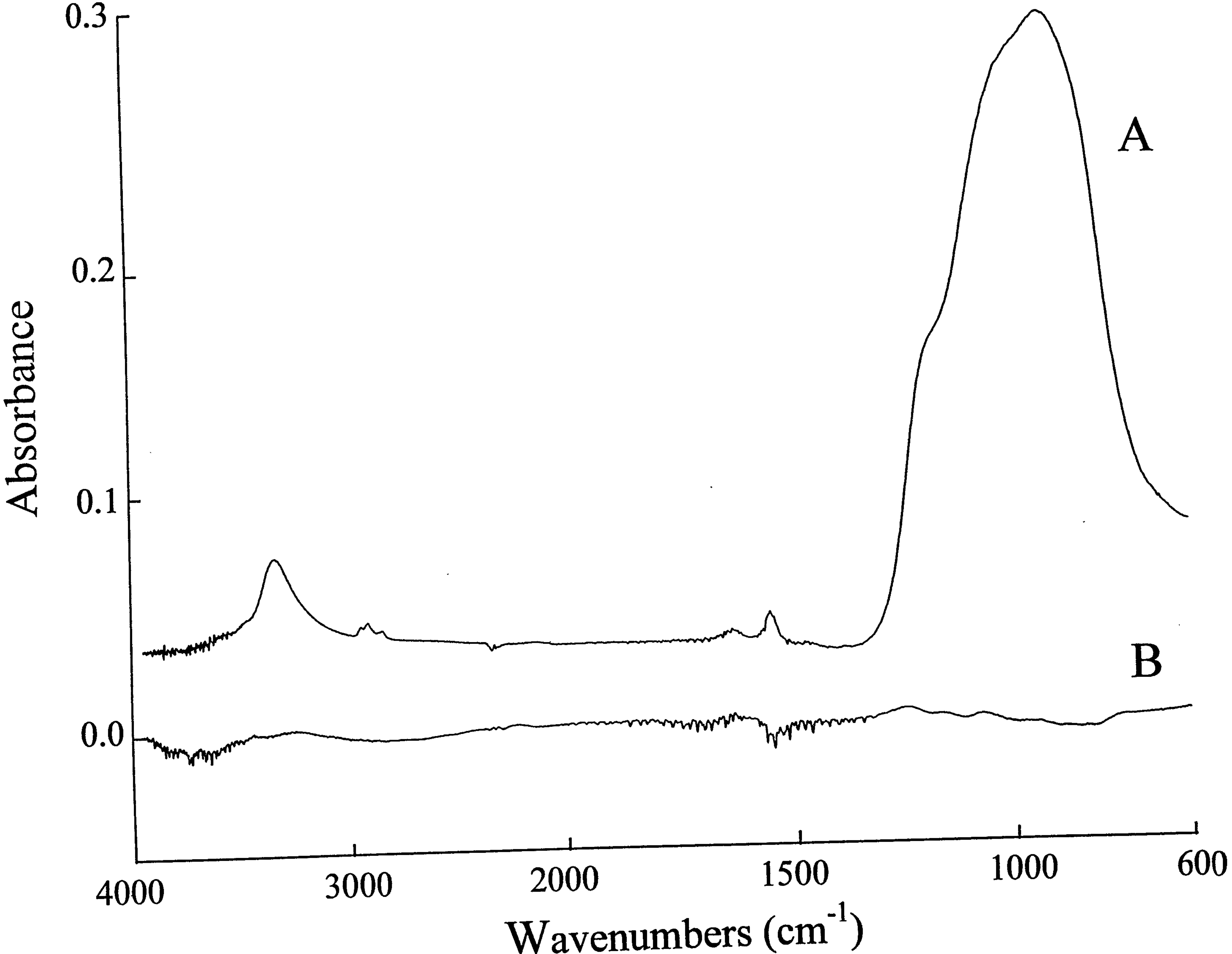
0.1
0.2
0.3
0.4
0.5
0.6
Particle diameter, nm
Plasma On-time, sec

5.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0.2
0.1
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Absorbance
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B
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1000
600
Wavenumbers (cm^{-1})