Morphologically Selective Low-Temperature Aqueous Synthesis of β-Ga_2O_3 Nanostructures in Pulsed Discharge Plasma Bubbles

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Abstract: Pulsed discharge plasma bubbles of varying process gases were utilized to synthesize β-Ga_2O_3 near room temperature. Oxygen-free plasmas formed well-defined “nanorice” structures of β-Ga_2O_3 whereas oxygen-containing plasmas lead to polydisperse microspheres formation. We propose this morphological selectivity depends on local •OH or •O concentrations which impact nanoparticle nucleation and growth kinetics.

1. Introduction

Beta gallium oxide (β-Ga_2O_3) is an ultrawide bandgap semi-conductor material of societal importance, however, the high calcination temperatures (>600°C) required to synthesize this specific polymorph lead to nanoparticle (NP) agglomeration, inhibiting control over desired NP characteristics [1-2]. An advantage of nonthermal plasmas for colloidal NP synthesis is that the plasma-liquid interface provides sufficient energy for the nucleation of metal oxides that are not otherwise possible under lower temperatures, thereby preventing NP agglomeration whilst maintaining nanoscale properties [3-4].

In this work, we demonstrate that β-Ga_2O_3 NPs can be synthesized at near room temperature with morphological selectivity using nonthermal plasma bubbles.

2. Methods

Plasma bubbles of pure gases (He, N_2, Ar, Air, O_2) were generated using nanosecond pulse discharges submerged in a 0.100M $Ga(NO_3)_3$ solution where the temperature was held constant at 65°C using a 200mL jacketed beaker with water circulation. For each plasma system, optical emission spectroscopy (OES) measurements were collected to determine reactive species. After 3 hours, the NPs were collected and characterized with scanning electron microscopy (SEM) to determine morphology and size distribution. Powder X-ray diffraction (pXRD) and transmission electron microscopy (TEM) were employed to confirm the presence β-Ga_2O_3 and GaOOH.

3. Results and Discussion

Figure 1 compares the morphology of β-Ga_2O_3 nanostructures resulting from different plasma conditions. Oxygen-free plasmas yielded nanorice structures with larger sized NPs produced from Argon plasma. With plasmas of increasing O_2 content, a larger amount of amorphous Ga_2O_3 spheroidal particles with fewer crystalline nanorice structures are observed. OES determined the concentration of •O and •OH to be key difference amongst different plasma conditions.

We propose that increased •O concentration from oxygen expedites growth kinetics of GaOOH by direct oxidation, forming spheroidal NPs whereas greater •OH concentration from He and Ar plasmas promotes the nucleation of more GaOOH seeds and anisotropic growth into β-Ga_2O_3 nanorice. We hypothesize that the formation of β-Ga_2O_3 under these lower temperatures is enabled by plasma bubble cavitations and local pressure effects enabling stability of the polymorph.

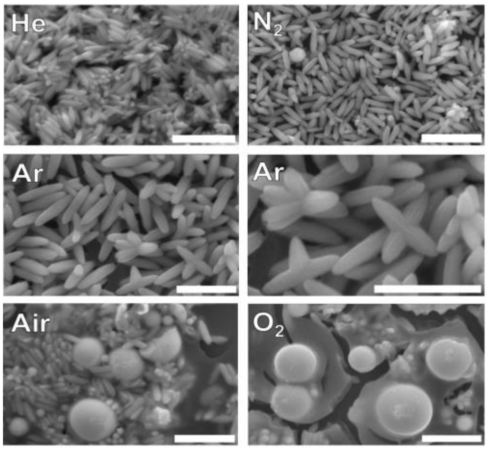

Figure 1. SEM images of β-Ga_2O_3 NPs formed by nonthermal plasma bubbles. Scale bar = 1000nm.

4. Conclusion

By modulating the electronic temperature and the oxidative environment at the plasma-liquid interface, our results show that plasma bubbles are a viable method to produce size and morphology controlled β-Ga_2O_3 NPs at lower temperatures compared to conventional high-temperature solvothermal methods. The introduction of O_2 promoted the formation of spherical NPs due to the increased generation of reactive oxygen species that accelerated nucleation and growth kinetics, leading to the formation of amorphous or poorly crystalline oxide phases.

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References

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