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Analytical Electron Microscopy of Silicon Nitride Nanostructures Synthesized from the Vapour Phase

[Microscopía electrónica analítica de nanoestructuras de nitruro de silicio sintetizadas a partir de la fase de vapor]

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Resumen

En el presente trabajo fueron estudiados por técnicas analíticas de microscopía electrónica el tamaño, morfología y composición del nitruro de silicio en polvo (Si3N4). Las muestras sintetizadas a 300 °C por precipitación de la reacción en fase vapor del SiCl4 y NH3, fueron analizadas utilizando Microscopia Electrónica de Barrido de Emisión de Campo (SEM) adquiriendo imágenes con electrones secundarios (SE) y electrones retrodispersados (BSE). Las fases cristalinas obtenidas por tratamiento térmico en una corriente de argón a 1500 °C se analizaron utilizando Microscopía Electrónica de Transmisión (TEM) que combina la difracción de electrones y la espectroscopia de rayos-x de dispersión de energía (EDS). Los resultados mostraron diferentes morfologías y una amplia distribución de tamaño del nitruro de silicio en polvo dependiendo del contenido de N, O y Si. El grado de aglomeración de las partículas están en el rango de micrómetros, sin embargo, el tamaño de las partículas individuales está en la escala nanométrica.

Palabras clave: Si_3N_4; Reacción en fase vapor; Nanoestructuras

Abstract

In the present study, the size, morphology and composition of the silicon nitride powder (Si3N4) were studied by analytical electron microscopy techniques. Samples synthesized at 300 °C by precipitation from the vapor phase reaction of SiCl4 and NH3 were analyzed using Field Emission Scanning Electron Microscopy (SEM) acquiring images with secondary electrons (SE) and back-scattered electrons (BSE). Their crystalline phases obtained by heat treatment in an argon stream at 1500 ºC were analyzed using Transmission Electron Microscopy (TEM) combining electron diffraction and energy dispersive X-ray spectroscopy (EDS). The results show different morphologies and a wide size distribution of the silicon nitride powder depending on the content of N, O and Si. The high degree of agglomeration shows particles in the micrometer range, however, the individual size of the particles is in the nanometer-scale

Keywords: Si_3N_4; Vapour phase reaction; Nanostructures.

1. Introduction

Silicon nitride, Si_3N_4 is a covalent compound with excellent physical and chemical properties such as corrosion resistance, low-specific weight and good thermal conductivity at ambient and elevated temperatures. Such properties are very attractive in application as advanced ceramics and in semiconductor devise (Kírstic, 2012). Nano sized amorphous silicon nitride powders can be synthesized at 300 °C by precipitation from the vapor phase reaction of $SiCl_4$ and NH_3 and Ar

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as carrier gas. Solid ammonium halogenide is formed as by-product, in addition to silicon nitride powder. When exposed to the atmosphere those powders are easily oxidized to silicon oxy-nitride. Crystalline phases are obtained by heat treatment in an argon stream at 1500 °C for 2 hours (Choy, 2001).

Silicon nitrate exists in four forms of solid structure, at the amorphous phase a-Si_3N_4 and the crystalline phases, trigonal α- Si_3N_4, hexagonal β- Si_3N_4 and at the recently discovered cubic phase γ- Si_3N_4 of high pressão (Ryley, 2000). In the amorphous phase it is widely used in the microelectronic industry as fine films and can be crystallized by heat treatment and different additive compositions. The α-phase occurs as a rare mineral (nierite) and the initial transformation temperature for the β-assume phase it is about 1400 ° C (Hierra, 2012). The thermodynamic study of the Si-O-N system shows that by heating Si_3N_4 in an oxidizing environment, a duplex oxide layer composed of silicon oxynitride (Si_2ON_2) and silicon nitride must form on its surface. Depending on the reaction kinetics and the oxidation duration, Si_2ON_2 in the oxide layer can almost completely oxidize SiO_2. The formation of this protective film is known as passive oxidation, and is the ability of Si_3N_4 ceramics to withstand high temperatures under oxidizing conditions without excessive oxidation. Si_3N_4 formation is favored with increasing temperature, and its tendency to oxidation is decreased (Ma, 2003).

2. Materials and Methods

Samples synthesized at 300 °C were analyzed using a FEI Magellan 400 Field Emission Scanning Electron Microscopy (SEM), operating under 3 kV, acquiring images with secondary electrons (SE) and back-scattered electrons (BSE). The structure and local of individual nanoparticles of the powder heated at 1500 °C was analyzed by means of transmission electron microscopy (TEM), combining electron diffraction and energy dispersive X-ray spectroscopy (EDS). The instrument JEOL 2100F 200kV was operated as a Scanning Transmission, STEM, and High-resolution, HRTEM microscope.

3. Results and discussions

SEM images in Figure 1 shows that nanoparticles with different morphology and large size distribution are formed, mainly as agglomerates, during the synthesis of the silicon nitride powder. In fact, nanoparticles with spheroidal, facetted cubic appearance and others of irregular shape are observed in Figure 1a. The individual size of the particles is in the nanometer-scale, the agglomerates, however, are in the micrometer range. In some cases, what appears to be a single coarse particle, as observed in a conventional SEM, is, in reality, an agglomerate of several nanoparticles adopting a cuboidal morphology which minimizes the overall surface energy, as shown on Figure 1b. When observing the surface of such agglomerate with a FEG SEM, as indicated in Figure 1c, the individual nanoparticles are well resolved.

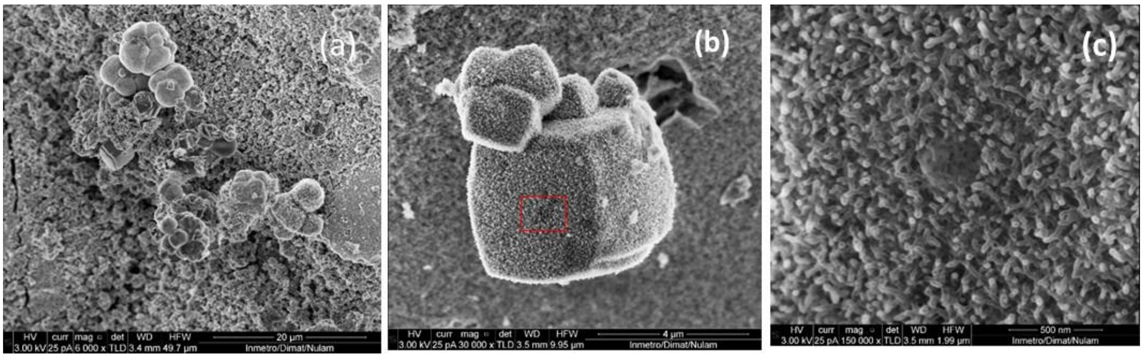

Figure 1. SEM images of the synthesized powder at 300 ºC (a) Agglomerated particles show different morphology and size distribution (b) Agglomerated nanoparticles (c) A higher local resolution shows the nano size of the individual grains.

The TEM images in Figure 2 illustrate the nature of a typical nanoparticle agglomerate of the powder heated at 1500 °C. Figure 2a is a STEM image with the corresponding elemental mapping of Si, O and N shown in Figure 2b. While these three elements appear equally distributed, attributing that most of the nanoparticles are Silicon oxy-nitrides in nature, a region in this image with N depletion is noticed.

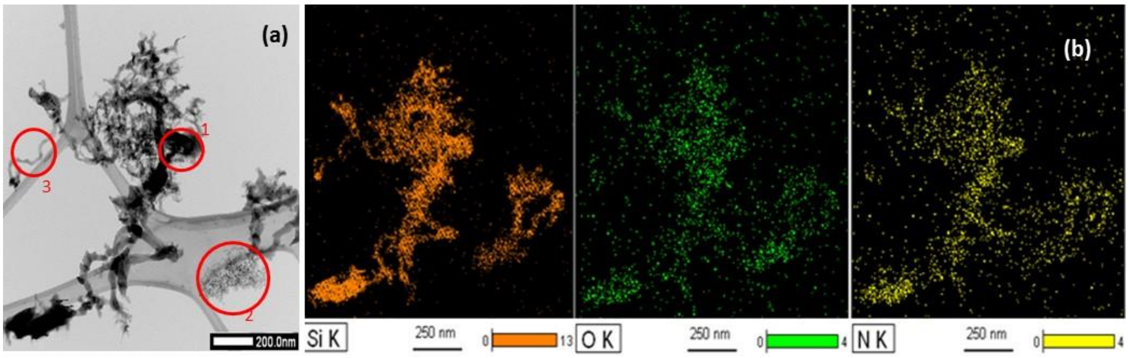

Figure 2. TEM analyses of silicon nitride powder heated at 1500 ªC, (a) STEM image shows the nanoparticles more prominently. (b) Elemental mapping of Si, O and N.

TEM images corroborates this information: bright field images (BF) obtained from three areas marked in the STEM image shows nanostructures of different morphology and their selected area diffraction pattern (SADP) indicates their local structure. Figure 3a shows the image and corresponding SADP of a faceted oxy-nitride single crystal in area 1; Figure 3b shows the image and SADP of an amorphous nano agglomerate where N is absent, characteristic of the SiO_2, in area 2; and in Figure 3c, area 3, the image and well-defined SADP of a nano ribbon.

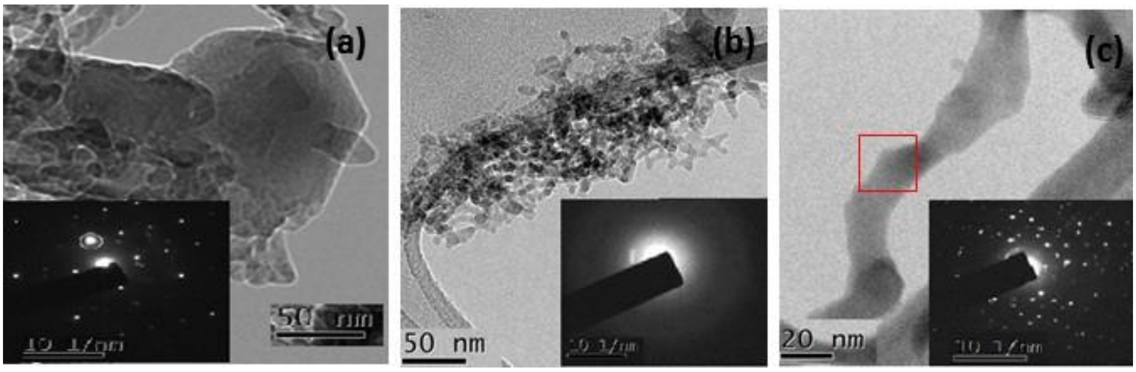

Figure 3. STEM BF images obtained from areas marked in the STEM image of the Figure 2. (a) Crystalline particles, (b) amorphous particles, and (c) poly crystalline particles respectively.

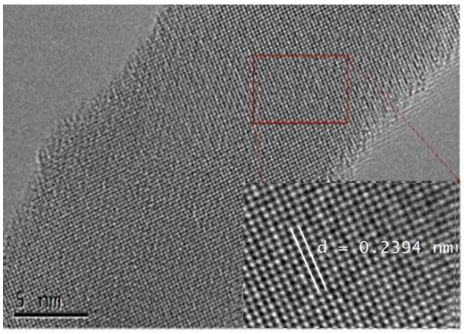

Figure 4. HRTEM image of the area marked on the nanoribbon.

The HRTEM image of the boxed area market on the nano ribbon shows a perfect crystal lattice oriented in <100> zone axis (Figure 4). The above-described example illustrates the heteronomous nature of the powder synthesized by this method, given rise to nano objects with different morphology and crystallinity depending upon the amount of N and O in the Si-rich compounds, from different oxy-nitrides to amorphous Si oxide.

4. Conclusions

The silicon nitride powder analyzed is composed of nanostructures with different morphologies and crystallinity, depending upon the quantity of N and O in the Si-rich compounds. Species with Si-O ligaments from different oxy-nitrides to amorphous Si oxide are observed. The silicon nitride powder could be regarded as a structure where excess vacancies are stabilized with oxygen. Crystalline structures were identified as α-Si_3N_4 obtained of the powder heated at 1500 ° C. The individual size of particles is in the nanometer-scale, the agglomerates, however, are in the micrometer range.

Acknowledgments

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