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Native oxide and hydroxides and their implications for bulk AlN crystal growth

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Abstract

Oxygen degrades the properties of AlN, thus producing bulk single crystals with low oxygen concentrations is an important goal. Most of the oxygen in bulk AlN single crystals grown by the sublimation-recondensation method originates from the hydroxides and oxides that spontaneously form on the surfaces of the AlN source powder. For a typical AlN powder with an average particle size of 1-2 microns, a 1-3 nm thick oxide and/or hydroxide can account for most of its oxygen (generally on the order of 1.0 wt%) and hydrogen (200-300 ppm). Heating the AlN powder source at 1950 °C for 10 h in a nitrogen atmosphere reduced its surface area by a factor of 160 (due to sintering), the oxygen concentration by 16, and the hydrogen concentration by 67. The difference in these reduction factors suggests some of the oxygen is dissolved into the bulk AlN with this heat treatment. By first annealing the AlN powder at a low temperature (950-1000 °C) for several hours before sintering at 1950 °C, the oxygen and hydrogen concentrations were reduced to lower levels. The low temperature treatment is effective eliminating oxygen and hydrogen from the surface of the powder, while high temperature sintering reduces the specific surface area of the source. The combination of heat treatments produced a source with oxygen and hydrogen concentrations as low as 0.015 wt% O (1.9×10^{19} atoms O cm^{-3}) and 1.7 ppm H (3.4×10^{18} atoms H cm^{-3}). Annealing becomes less effective at removing oxygen and hydrogen with longer heat treatments, suggesting there is a minimum oxygen concentration that can be produced with this method.

Keywords: A1. Impurities; A1. Purification; A2. Growth from vapors; B1. Nitrides; B2. Semiconducting Aluminum Compounds

PACS: 81.05. Ea; 81.10 Bk; 81.20 Ym

Introduction

Aluminum nitride single crystals have several advantages over sapphire and silicon carbide as substrates employing $Al_xGa_{1-x}N$ epitaxial layers for electronic and optoelectronic devices.[1-5] Aluminum nitride has the same crystal structure (i.e. wurtzite) as all compositions of $Al_xGa_{1-x}N$, thus epitaxy in any crystal orientation should be possible on AlN. Aluminum nitride's thermal conductivity (3.2 W/cm·K)[6] is 6-7 times higher than that of sapphire; thus AlN is better at dissipating heat generated by devices. Unlike silicon carbide, AlN can be transparent to ultraviolet light, so UV light generated by a device would not be lost absorption on AlN substrate. AlN does not contain elements that are potential dopants in the epitaxial layers, as oxygen from sapphire or silicon or carbon from silicon carbide are.

Most importantly of these three substrates, AlN has the smallest lattice constant mismatch with $Al_xGa_{1-x}N$. By employing AlN substrates, it may be possible to prepare epitaxial layers without any high dislocation density buffer layer. Consequently, using AlN single crystal substrates should reduce the density of dislocations in $Al_xGa_{1-x}N$ epitaxial layers. This will improve the efficiency of light emitting diodes, especially those emitting at wavelengths shorter than 280 nm. The beneficial effects can be dramatic: Mymrin *et al* [7] predicted that reducing the dislocation density in epitaxial $Al_xGa_{1-x}N$ devices layers will increase the external quantum efficiency of UV LEDs by two orders of magnitude. Such an increase in efficiency would help to make $Al_xGa_{1-x}N$ UV-LEDs commercially viable.

The largest and highest quality bulk AlN single crystals are grown by the sublimation-recombination process.[3,4,8] This method is based on driving the reaction $AlN(s) = Al(v) + ½N_2$ forward in the source zone and in reverse in the crystal growth zone. The source is typically AlN powder or a sintered polycrystal, and sublimation occurs at temperatures greater than 1900 °C. Over the last decade, this method has produced large, high quality AlN crystals with relatively low etch pit densities (10^4-10^5 cm^2) after defect selective etching.[9,10]

One problem with bulk AlN crystals produced by the sublimation-recombination process is their high oxygen concentration, typically on the order of 10^{19} O atoms cm^{-3}.[11,12] Oxygen adversely affects the properties, crystal quality, and surface morphology of the AlN crystals.[13-16] At low concentrations, oxygen promotes the formation of Al vacancies which significantly reduces AlN's thermal conductivity.[13] With increasing oxygen concentration and hence Al vacancy concentrations, the Al vacancies coalesce, forming stacking faults, inversion domains, and more extended defects.[14] Furthermore, the release of oxygen from the substrate to the film during epitaxial growth could interfere with efforts to control the electrical properties of the film by impurity doping.

The present paper considers the origin of oxygen in AlN powders. Native surface oxides and hydroxide that spontaneously form on the AlN powder particles are identified as the main source of oxygen. Reducing the surface area of the AlN source is shown to be effective at reducing the oxygen concentration. The evolution of the surface area of the source with sintering is measured. The impact of annealing and sintering - often employed to reduce the concentrations of oxygen and hydrogen in the source material- is examined. Finally, recommendations concerning processing to reduce the oxygen and hydrogen in the AlN source material before it is employed in crystal growth are made.

Background
Aluminum has a strong affinity for oxygen, hence the surfaces of most solid aluminum compounds are covered with a native oxide or hydroxide.[17] Oxidation occurs in the presence of oxygen; hydroxidation occurs when aluminum oxides react with water vapor in air. The amorphous thin film that forms may be a mixture of one or several aluminum-oxygen-hydrogen compounds such as aluminum trihydroxide ($Al(OH)_3$), aluminum oxide hydroxide (AlOOH, or $Al_2O_3{\cdot}H_2O$), or aluminum oxide (Al_2O_3).[18] The Gibbs free energy of formation of these compounds at room temperature have large negative values, so there is a strong tendency for them to form. The diffusion of oxygen, water, and aluminum through the film is slow at room temperature, thus growth of the native oxide/hydroxide is self-limited: oxidation and hydroxidation ceases after a film of a few nanometers is formed.

Several studies suggest that the main native thin film that forms on AlN exposed to ambient air is AlOOH.[18,19] Its formation occurs rapidly, within a few minutes. Panchula and Ying [18] followed the formation of native hydroxides on freshly prepared nanocrystalline AlN upon exposure to oxygen and water vapor in ambient air by photo-acoustic Fourier transform infrared spectroscopy. Surface adsorbed species were readily detected due to the high surface area of their powder (250 m^2/g). Before exposure to air, the presence of NH_2, Al-H, and adsorbed CN or HCN (the latter two formed during the synthesis of the powder) was inferred from the spectra. After exposure to air for 5 minutes, the changing spectra indicated AlOOH was forming, with the physisorption or weak chemisorption of water, and a diminished signal from CN/HCN due to desorption or reaction with water. Additional changes in the spectra indicating further reactions with oxygen and water occurred during the 18 hours of their study.

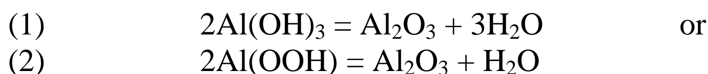
Several studies have attempted to directly measure the thickness of the native oxide/hydroxide on AlN. Slack and McNelly [8] reported that an oxide 5.0 to 10.0 nm forms on AlN in one day at room temperature based on neutron activation analysis of powders and optical ellipsometry on single crystals. For comparison, they reported a literature value for aluminum metal of 3.0 nm. Dutta and Mitra [20] measured an α-Al_2O_3 2-3 nm thick, formed within minutes on freshly cleaned AlN at room temperature. Measuring the native oxide/hydroxide of several AlN powders, Kameshima *et al* [21] reported that the oxide/hydroxide thickness was dependent on how the AlN powder was synthesized. From x-ray excited Auger electron spectrum (XANES) measurements, Kameshima *et al* [21] concluded that the oxide thickness of AlN powders produced by carbothermal means was twice as thick (1.1 nm) as those found on AlN powders produced by direct nitridation (0.5-0.6 nm). Also using XPS, Dalmau *et al* [19] concluded that the limiting thickness of AlOOH on AlN (0001) exposed to air was 1.2 nm.

Measurements of the native oxide thickness on AlN have also become available as a byproduct of the development and characterization of AlN nanoparticles. Examing published high resolution transmission electron micrographs of AlN nanoparticles by Panchula and Yang,[18] Shen *et al*,[22] Kim,[23] and others suggests that the native oxide/hydroxide is 1.5 nm to 3 nm thick.

Sintering has been developed as a means to reduce the concentration of oxygen in AlN powders before it is used to grow AlN crystals. Bickermann *et al* [11] accomplished this by heating their AlN source to partially sublime the material. They noted that an oxygen-rich layer was the

initial product formed in the crystal growth zone when an AlN source is sublimed. This suggests that in an oxygen-free nitrogen ambient, aluminum-oxygen species are more volatile than AlN.

A simple procedure for reducing the oxygen concentration in AlN powder is heating in either a vacuum or under nitrogen. If the oxygen is present as AlOOH or $Al(OH)_3$, reactions involving hydrogen may also be effective at removing oxygen from AlN powder via the formation of water. In this case, the reactions might involve



(1) $2Al(OH)_3 = Al_2O_3 + 3H_2O$ or

(2) $2Al(OOH) = Al_2O_3 + H_2O$

In a study of water desorption from AlN powders by temperature program desorption (TPD) Saito *et al* [24] detected significant amounts of water desorbing between 200 °C to 450 °C. Their study and a subsequent study by Li *et al* [25] supports the probability of reactions 1 and 2 occurring. Similar conclusions were drawn from XPS analysis by Dalmau *et al*;[19] an oxygen peak characteristic of a hydroxide was reduced by annealing for 6 h from 260 °C to 830 °C under ultrahigh vacuum. The intensity of XPS oxygen peaks changed in a manner indicating a shift in the surface composition from AlOOH toward Al_2O_3 with increasing temperature.[19]

At sufficiently high temperatures (more than 1500 °C), in the presence of Al vapor (which is produced by the sublimation of AlN), the oxide can be removed by forming volatile oxygen species.[26] The most probable reaction is

(3) $Al_2O_3 + 4\ Al(g) = 3Al_2O$.

This reaction may be involved in the formation of the oxygen-rich material that Bickermann *et al*[11] observed.

Experimental

In this study, the removal of oxygen from the AlN source was examined. The aluminum nitride powder used in these experiments consisted of spherical particles, with an average diameter of 1.5 µm. The manufacturer reported surface area for this powder was 3.4 m^2/g, with 0.9 wt% oxygen and 0.06 wt% carbon as the main impurities.

The AlN powders were treated in two ways to reduce the surface area and oxygen concentration. In one set of experiments, the AlN powder was held at approximately 1950 °C (sintered) for times ranging from 2 to 20 hours in a nitrogen ambient. In a second set of experiments, the AlN was first held at 960 °C to 1000 °C (annealed) for 2 h to 10 h in a vacuum, and then was sintered at 1920 °C for 2 h to 10 h in nitrogen, the amount of time for each sample being equal to the low temperature annealing time. The source was located in a temperature gradient of approximately 5 °C/cm, which cause it to lose mass via sublimation. The mass of the source was measured before and after the heat treatments, to determine the percent of mass change. All experiments were performed using a tungsten crucible in a resistantly heated all tungsten furnace.

The specific surface areas of the original powder and the powders after heat treatments were measured by the multi-point BET (Brunauer, Emmet, and Teller) method using krypton gas, the

preferred gas for low surface area materials. The oxygen and hydrogen concentrations were measured by the inert gas fusion technique, commonly referred to as LECO analysis. Transmission electron microscopy (TEM) specimens were prepared from the AlN powders. The particles were suspended in methanol and then ultrasonicated for three minutes to separate the particles. A suspension drop was placed on a holey carbon film coated on a Cu grid and left to dry. A Hitachi H8100 TEM operating at 200kV was used to take high resolution micrographs to determine the thickness of the native oxide layer.

Results

The source for most AlN single crystal growth studies is AlN powder composed of small particles that are less than 1 to 2 microns in diameter. The surface area of common commercially available AlN powders is typically between 2 to 4 m^2/g, which is substantially larger than the minimum possible. Based on the density of AlN (3.261 g/cm^3), the minimum surface area (assuming the shape of a sphere) for 1.0 gram of fully dense AlN is $2.2 \cdot 10^{-4}$ m^2/g; four orders of magnitude less than that of the powders. Thus, because powders have large surface areas, even though the oxide or hydroxide layer is quite thin, the powders will inherently contain a high concentration of oxygen.

The maximum native oxide thickness can also be estimated by knowing the surface area of the powder (or estimating the surface area from the average powder particle diameter, assuming the particle is spherical) and its bulk oxygen concentration. By knowing the powder's surface area, oxygen concentration, and the densities of the oxide (assume to be 3.98 g/cm^3), the maximum native oxide film thickness can be calculated by assuming all oxygen resides in the film. Using the oxygen concentrations and surface areas reported by commercial vendors, and the characteristics for several AlN powders reported by Weimer *et al*,[26] a range of maximum oxide thicknesses from 1.3 to 4.0 nm was deduced. Assuming the thin film is all $Al(OH)_3$ (density of 2.42 g/cm^3) instead, increases this thickness value by only 25%. Thus, a minimum oxide/hydroxide thickness for AlN exposed to ambient air is 1.3 nm, and a typical value is 2-3 nm.

The as-received AlN powder particles employed in the present study were approximately spherical in shape (Fig. 1.a). The thickness of the oxide/hydroxide on the surface of one of these particles was measured as 2.0 nm by high resolution transmission electron microscopy (Fig. 1.b). This value is similar to those previously measured in TEM studies of AlN nanowires and other nanoparticles.[18,22,23] The initial oxygen and hydrogen concentrations of the as-received AlN powders in the present study were 0.82 wt% and 237 ppm respectively (1.0×10^{21} O/cm^3 and 4.7×10^{20} H/cm^3), as measured by inert gas fusion. The atomic ratio of O/H is 2.2 suggesting most of the oxygen is present as AlOOH, since it has a O/H ratio of 2.0.

The specific surface area of the AlN source was measured as a function of the mass sublimed (the percent reduction in mass) and is presented in Figure 2. The original surface area of the as-received powder was 3.5 m^2/g, which is nearly the same as that specified by the manufacturer. With just a 3.5% mass reduction (2 h sintering at 1950 °C), the surface area drops sharply by a factor of 30. With additional sublimation, the specific surface area decreases more gradually, by another factor of 5 for a 19.3% total mass reduction. In all, the surface area was reduced by a factor of 160 after sintering at 1950 °C for 10 hours in nitrogen. Despite this significant

reduction, the specific surface area of the source was still a hundred times larger than the minimum possible for AlN. Scanning electron micrographs reveal this change in surface area occurred with the agglomeration of particles and an increase in their average size (Fig. 3).

The concentrations of oxygen and hydrogen in the AlN source were also significantly reduced by sintering at 1950 °C. With a 16.5 % mass reduction by sublimation (10 h), the oxygen in the source was reduced from 0.824 wt% O to 0.049 wt% O, at factor of 16.8 (Fig. 4). With the same mass reduction, the hydrogen concentration in the AlN source changed from 237 ppm originally, to 3.5 ppm. The factor by which the hydrogen was reduced is larger than that for oxygen (68 times), but it is still less than the factor by which the surface area was reduced.

To reduce the oxygen and hydrogen concentrations even further, a series of sources were prepared in a two step process, annealing first at 960 °C in a vacuum before sintering at 1950 °C in nitrogen. The goal was to decompose the hydroxide and desorb water at a low temperature, as suggested by the work of Saito *et al.*[24] Heating at this low temperature should remove much of the surface oxygen and hydrogen without creating voids with internal surfaces that contain oxygen and hydroxides. Using this procedure, the oxygen and hydrogen concentrations were further reduced by factors of 2 and 2.5 in comparison to the cases of directly heating to the sintering temperature. The minimum oxygen and hydrogen concentrations in the sources were 0.015 wt% O (1.9×10^{19} cm^{-3}) and 1.7 ppm H (3.4×10^{18} cm^{-3}). Despite the additional low temperature heating, the rate of mass change with time was nearly identical to the case of sintering alone.

Discussion

Subliming roughly 15% of the original AlN powder source mass reduced the surface area from 3.5 m^2/g to 0.02 m^2/g, a factor of 175. By heating directly to 1950 °C and subliming roughly 15% of the original source mass, the O concentration changed from 0.8 wt% to 0.05 wt%, and the H concentration changed from 240 ppm to 4 ppm, reduction factors of 16 and 60 respectively.

If oxygen were present only in a 2 nm thick layer of hydroxide (AlOOH) on the surface of the AlN source after this heat treatment, the oxygen concentration would have been 0.0064 wt% and the hydrogen concentration would have been 2.0 ppm. Since it is unlikely that the native oxide that forms on the heat treated AlN is significantly thicker than the original powder, this suggests that the oxygen is no longer confined principally to the surface, but was contained within the AlN, possibly dissolved into the bulk AlN or trapped at internal surfaces of voids.

Including a low temperature heat treatment before high temperature annealing reduced the oxygen and hydrogen concentrations more than heating directly to 1950 °C. With a low temperature annealing step, for a 15% reduction in the source mass, the oxygen and hydrogen concentrations were 0.02 wt% O and 1.9 ppm H, further reductions in concentrations by factors of roughly 2-2.5. Clearly, the low temperature heating helped to remove the oxygen and hydrogen over what was possible by heating directly to 1950 °C. The low temperature heat

treatment probably removes the oxygen and hydrogen via water desorption. This occurs without sintering, which can create voids in the material which trap the impurities.

Still, even with the low temperature annealing step, the remaining oxygen concentration exceeded that which was expected from a surface hydroxide layer alone. After sintering, the oxygen to hydrogen ratio had increased to 8.8. This change in the O/H ratio also suggests that some of the oxygen is dissolved in the AlN, if all the remaining hydrogen is present at the surface.

The decreases in the rates of oxygen removal and surface area reduction with increasing annealing time suggest that there is a minimum oxygen concentration that sintering can achieve. There is an asymptotic approach to limits of both the surface area and the oxygen concentration with time. These limits on the source material will in turn set a minimum oxygen concentration in the AlN crystals grown from these sources. Therefore, further reductions in the oxygen concentration in AlN crystals will require a different approach such using different source materials.

Conclusions

Most of the oxygen in the AlN powder sources employed for bulk crystal growth is initially present as a surface hydroxide, most likely AlOOH. The high surface area of powders limits the minimum oxygen concentrations possible in the original source to relatively high values, on the order of 1.0 wt% oxygen. Heating to partially sublime the source reduces the surface area (via sintering) and the oxygen and hydrogen concentrations. The lowest concentrations of hydrogen and oxygen are achieved in a two step process, by first annealing the AlN source at a low temperature (<1000 °C) in a vacuum to remove the hydroxides and adsorbed water vapor, then sintering at a high temperature (1950 °C) in nitrogen. Nevertheless, there is a minimum oxygen concentration that can be achieved by sintering; longer sintering time or the partial sublimation of more material becomes increasingly less effective at removing oxygen. This suggests that alternate approaches such as employing different AlN sources will be required to grow AlN crystals with low oxygen concentrations.

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Figure Captions

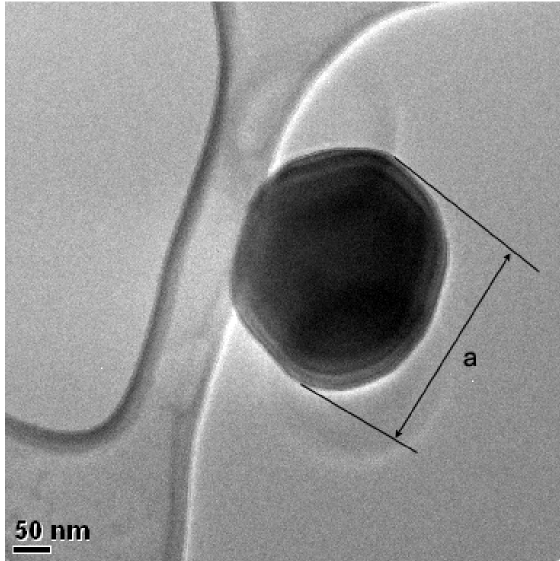
Figure 1 Images of the as-received AlN powder employed in this study. (a) Transmission electron micrograph of an individual AlN particle. (b) High resolution TEM image of the native oxide/hydroxide on the AlN powder particle.

Figure 2 Specific surface area of the AlN source as a function of the mass sublimed at 1950 °C under a nitrogen pressure of 613 torr.

Figure 3 Scanning electron micrographs of the AlN source: (a) the as-received powder, and (b) the source after sintering for 5 hours at 1950 °C. The average particle size increases with sintering. The scale bar is 5.0 microns.

Figure 4 The oxygen concentration of the AlN source as function of the mass sublimed at 1950 °C. Open circles and dashed line are from sources that were heated directly to 1950 °C, closed circles and solid line are from sources that were annealed at 960 °C before sintering at 1950 °C.

Figure 5 The hydrogen concentration of the AlN sources as a function of the mass sublimed at 1950 °C. Open circles and dashed line are from sources that were heated directly to 1950 °C, closed circles and solid line are from sources that were annealed at 960 °C before sintering at 1950 °C.



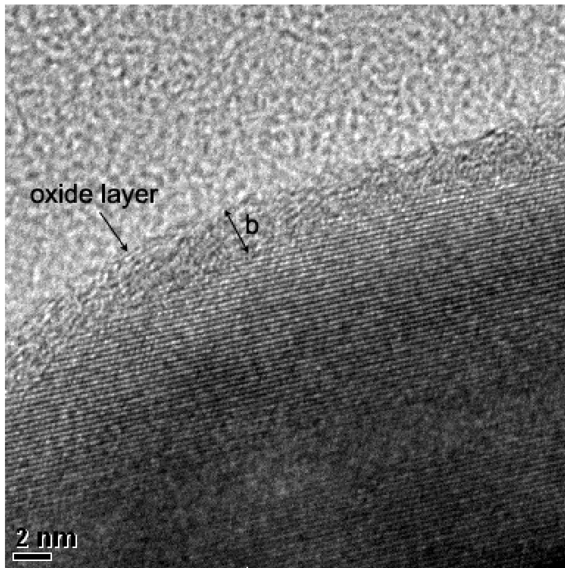


Figure 1

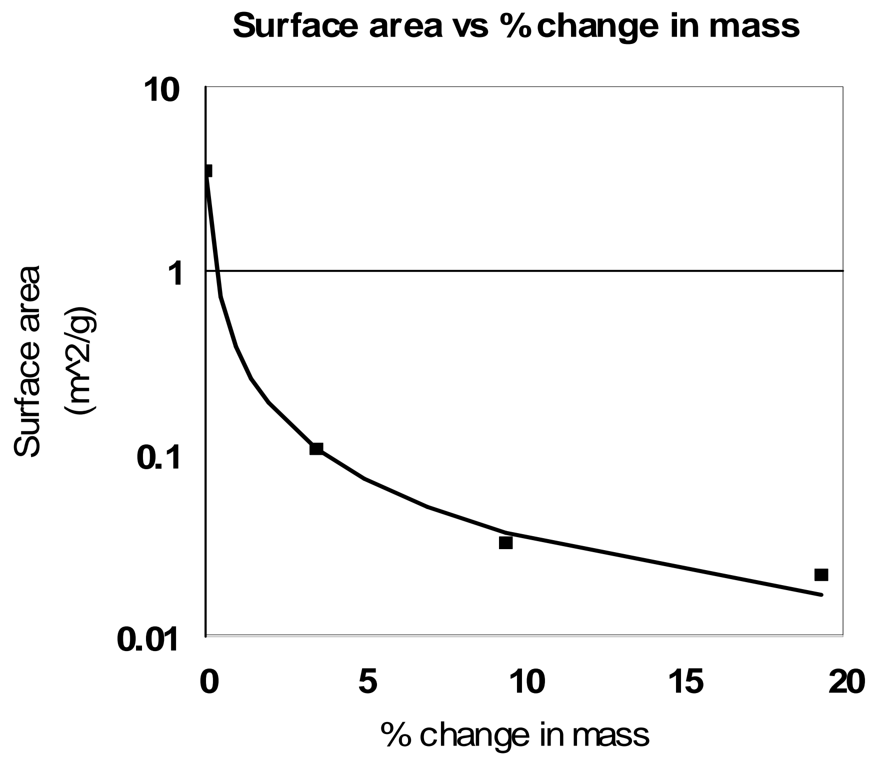
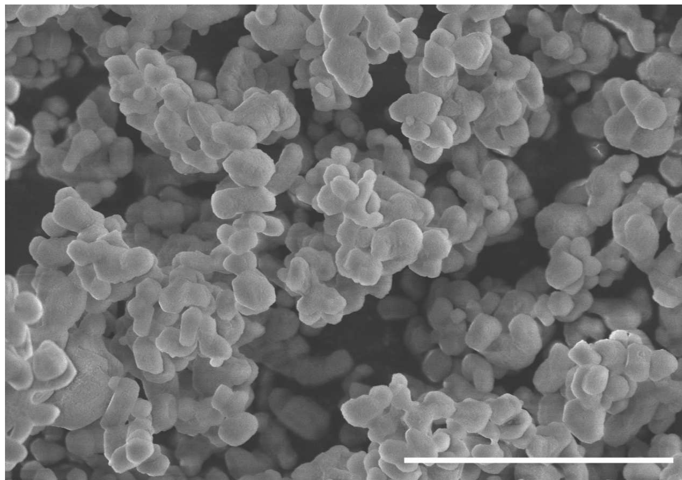


Figure 2.



(a)

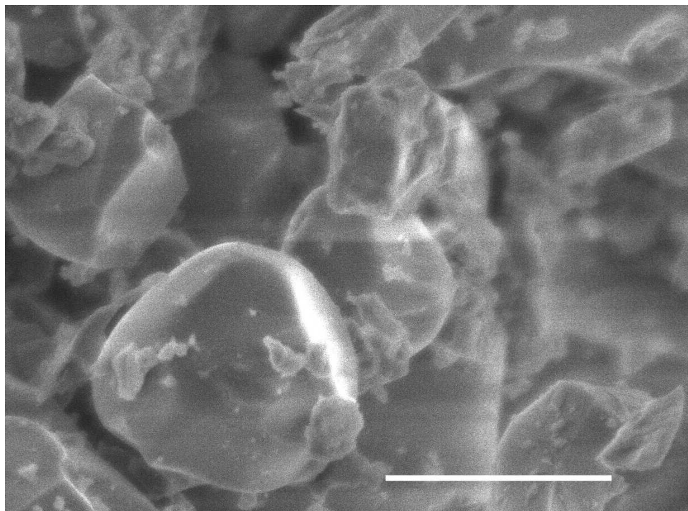


Figure 3

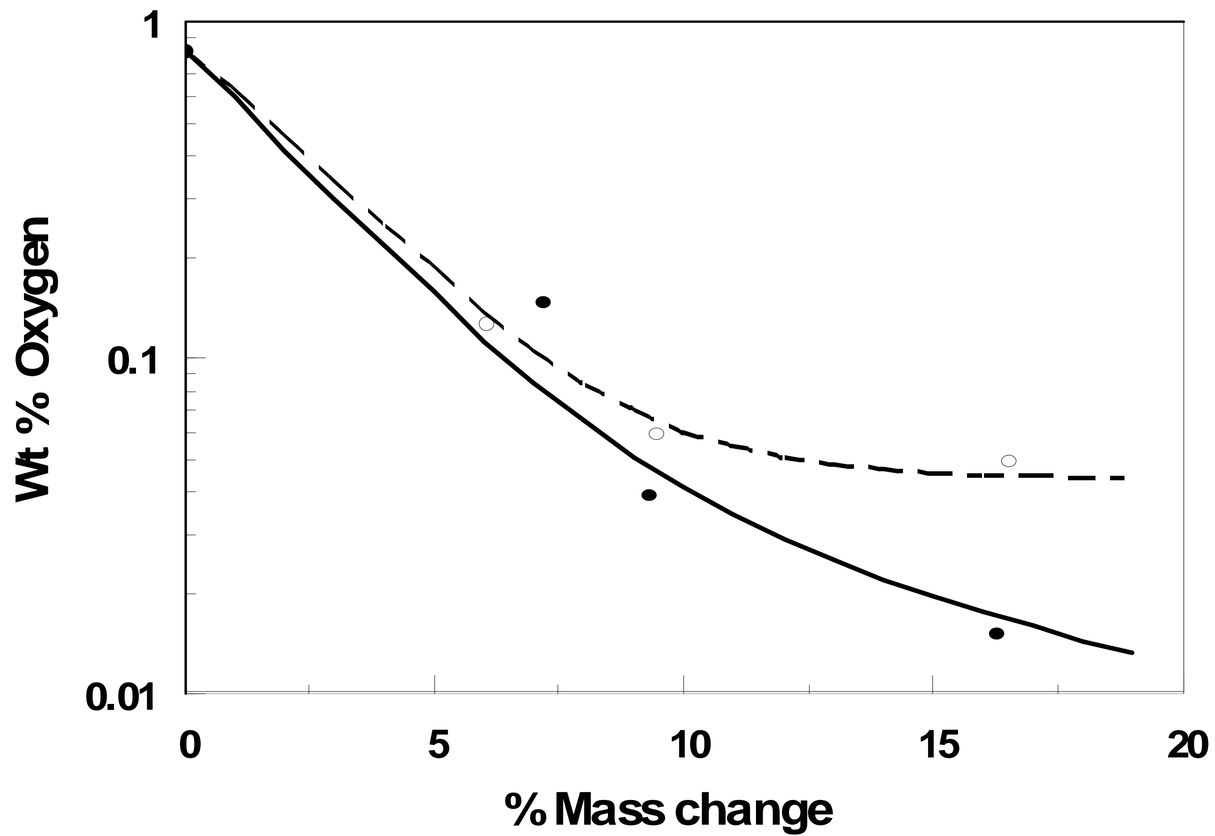


Figure 4

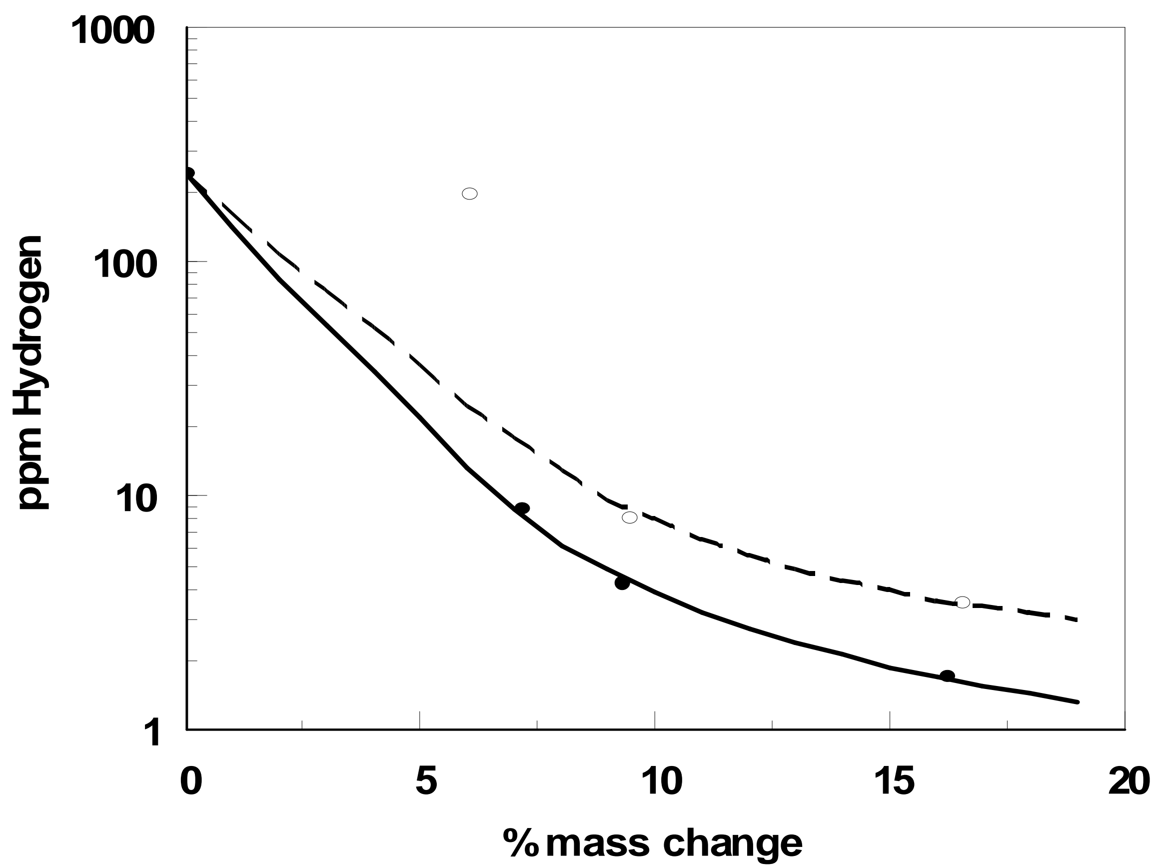


Figure 5