Electrochemical Synthesis of Ceramic Materials. 4. Electrophoretic Deposition of Metal Nitride Ceramic Precursors

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We have prepared metal nitride ceramic precursors by anodic dissolution of the corresponding metal in liquid NH_3 electrolyte solutions and then deposited coatings of these precursors onto n-Si substrates by electrophoresis. X-ray diffraction and electron microscopy indicate that calcination of the precursor-coated substrates yields coatings of AlN, δ-NbN, and Ni_3N. Precursor coatings are formed by applying fields greater than 10 V/cm between electrodes in a CH_3CN suspension of the precursor. The positively charged precursor particles deposit selectively on the cathode. Subsequent calcination in flowing NH_3 or Ar yields the metal nitride coating. The Ni_3N coating was prepared by calcining the precursor at 375 °C in NH_3, while the AlN and NbN precursor coatings were prepared by calcination at 1100 °C in NH_3 and 800 °C in Ar, respectively.

Introduction

In this article we discuss a new method for coating conductive substrates with metal nitride thin films. The precursors for the coatings, which are derived from a process involving anodic dissolution of metals in liquid NH_3/electrolyte solutions, are electrophoretically deposited onto n-Si cathodes from suspensions in CH_3CN.[1−4] Calcination of the precursor-coated cathodes in flowing NH_3 or Ar yields metal nitride ceramic coatings. In this paper, we briefly describe this simple method for preparing non-oxide ceramic coatings and provide preliminary X-ray diffraction (XRD) and scanning electron microscopy (SEM) data for AlN, δ-NbN, and Ni_3N coatings.

Metal nitride films and coatings have a range of important applications. For example, due to its superior thermal conductivity and good thermal expansion match to Si, AlN is a candidate to replace Al_2O_3 as an electrical insulator in semiconductor devices.[5−8] δ-NbN is used in SQUIDS and Josephson junctions because it is a type II superconductor with a relatively high superconducting transition temperature (T_c) of 17.3 K and a high superconducting current capacity (J_c) of $\sim 10^5$ A/cm^2 at 4.2 K and 100 kOe.[9,10]

There are many methods for preparing metal nitride coatings, including chemical vapor deposition (CVD), physical vapor deposition (PVD), and reactive sputtering.[11−16] Electrophoretic deposition of metal nitride precursors is a new approach for preparing nitride ceramic coatings. The advantages of this method are that it does not require expensive equipment, and it has the potential for coating irregularly shaped objects. These advantages have previously been recognized and used to prepare other types of ceramic coatings,[17−23] and a recent review of this subject provides insight into both the experimental and theoretical development of this approach.[17] Preceding our work, Moritiz and Reetz described a process for electrophoretically depositing AlN coatings on Pt substrates.[23] They began with poly(acrylic acid)-coated AlN powders emulsified in ethanol. Electrophoretic deposition resulted in a $[CH_2CH(COOH)]_n$/AlN coating on the anode, which was sintered at 1850 °C in N_2 to yield an AlN coating. This strategy is distinct from the approach we describe, in that we do not add charged compounds to the metal nitride precursor to render it suitable for electrophoretic deposition. This eliminates an experimental step and a major source of C and O contamination, which seriously compromises the desirable electrical properties

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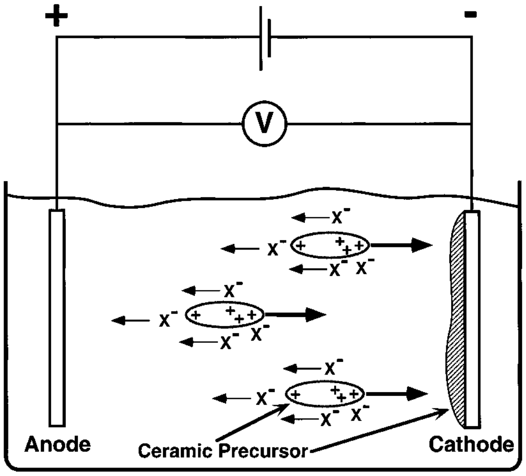
Scheme 1



of AlN. Moreover, the calcination temperatures required to convert the precursor to the metal nitrides are relatively low using the new method described here, and therefore it is compatible with Si processing technology.

We previously described an electrochemical approach for preparing metal nitride ceramic precursors, but the essential aspects of the synthesis are briefly reviewed here.[1-4] Anodic dissolution of metals in NH_3 yields metal ions (M^{n+}). At the cathode, NH_3 is reduced to NH_2^-, which we believe reacts with M^{n+} to yield a metal amide. Some metal amides condense spontaneously through loss of NH_3 and formation of bridging NH groups to form an insoluble metal–amide–imide precursor.[2,3] Several transition-metal ions react directly with NH_3 by ammonolysis to yield similar materials.[4,24,25]

We believe the metal–amide–imide precursor precipitates as a salt from the electrolyte solution before or during evaporation of NH_3, so it is charged and undergoes electrophoretic migration in an electric field and deposits on the cathode (Scheme 1). It is also possible that the precursor forms charged colloids due to charge transfer between the precursor particles and the solvent.[26] During calcination the precursor coatings are thermally converted to metal nitride ceramic coatings and impurities sublime from the films.[1-4]

Experimental Section

The precursor powders were prepared by anodic dissolution of metals in liquid NH_3 as previously described.[1-4] A 1 × 4 cm Al anode and a 1 × 4 cm, n-doped Si (100) cathode (n-Si) were cleaned with soap and water, rinsed with deionized H_2O, and dried under a stream of N_2. To improve adhesion between the substrate and the coating, we etched the n-Si substrates in KOH prior to deposition. KOH cleaning could improve adhesion by either increasing the substrate surface area or improving the interfacial free energy match between the substrate and the coating.

Inside a N_2 glovebox, ~0.3 g of the precursor was ground to a fine powder in an agate mortar and placed in a 100 mL beaker. Next, ~80 mL of CH_3CN was added to the beaker, and it was covered with paraffin film prior to removal from the N_2 box. We used CH_3CN as the solvent because Br^- and Cl^- salts of the precursor are slightly soluble in it. Outside the N_2 box, the paraffin film was removed and replaced within a few seconds by a lid containing a small hole for N_2 purging and two slots through which the electrodes could be passed. N_2 purging began immediately after placing the lid on the beaker to minimize O_2 and H_2O contamination, since the precursor slowly hydrolyzes in the presence of H_2O. The electrodes, which had an active area of about 3 cm^2, were positioned in the beaker with their surfaces parallel to each other and ~1 cm apart. A deposit formed at the cathode when sufficient voltage was applied between the electrodes.

After deposition the cathode was removed from the beaker, placed in a quartz calcination tube and slowly (0.50 °C/min) heated to the desired temperature in flowing gas (~5 mL/min). The calcined coatings were removed from the calcination tube in the N_2-containing box and stored there prior to analysis. The films were analyzed using a Sintag PAD V powder X-ray diffractometer. We attempted to analyze the coatings using standard methods, but much better results were obtained using a grazing-angle geometry. For most measurements, the X-ray source was held at 87° from the surface normal and the detector was stepped from 20° to 100° 2θ at a rate of 0.04°/step and a counting time of 3 s/step. This geometry results in the presence of two artifacts in the spectra. First, the thickness of the substrate results in a peak offset, which is especially noticeable at high 2θ. Second, in some spectra (depending on the rotational angle of the substrate) we observe the (311) reflection of the Si substrate. SEM micrographs of the coatings were obtained using a JEOL T330A microscope.

Results and Discussion

Immediately following electrophoretic deposition, the AlN precursor coating is smooth and white. However, after calcination the coatings crack, and we observe sublimation products at the end of the calcination tube. The upper and lower images shown in Figure 1 are top- and side-view SEM micrographs, respectively, of a coating prepared by depositing the AlN precursor at 150 V for 1 min and then calcining at 1100 °C. The micrographs indicate that the coating is rough; however, the interface between the ceramic coating and the n-Si substrate is flat. We found that it was possible to remove the coatings by scraping them, but they could not be removed using less drastic methods and they did not delaminate upon drying. The micrographs also reveal that the coating is >5 μm thick and composed of particles that are as large as 5 μm. The total weight of the coated substrate decreased by about 60% during calcination, which is consistent with sublimation of impurities and pyrolysis of the precursor. This rather large weight loss accounts for cracking of the film.

Figure 2a is an XRD spectrum of the AlN coating shown in Figure 1, and Figure 2b is the same spectrum after the application of a 25-point smoothing routine. Figure 2c is a conventional XRD spectrum of the AlN coating after it was scraped from the n-Si substrate. The JCPDS file-card spectrum for AlN, which is shown at the bottom of Figure 2, confirms that it is composed of randomly oriented AlN crystallites.[27] The slight offset of the peaks in Figure 2a,b, compared to the JCPDS file-card pattern, is due to a slight sample displacement caused by the finite thickness of the n-Si substrate.[28] The inset in Figure 2 is a plot of the mass of electrophoretically deposited AlN precursor as a function of

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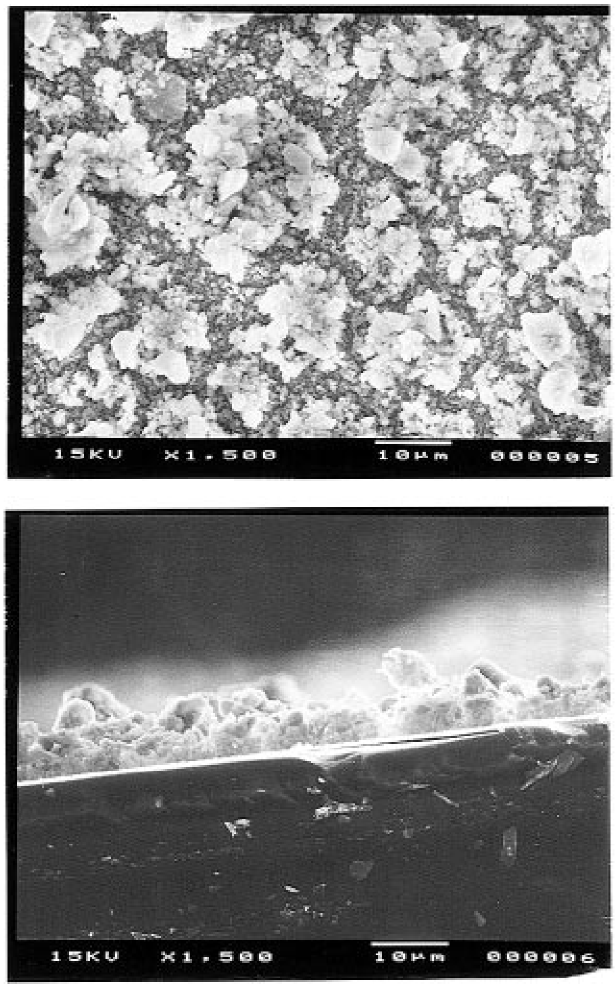

Figure 1. SEM micrographs of an AlN coating on an n-Si cathode substrate. The top micrograph is a view of the coating normal to the surface, and the bottom micrograph is an edge view of the coating at a cleaved side of the sample.

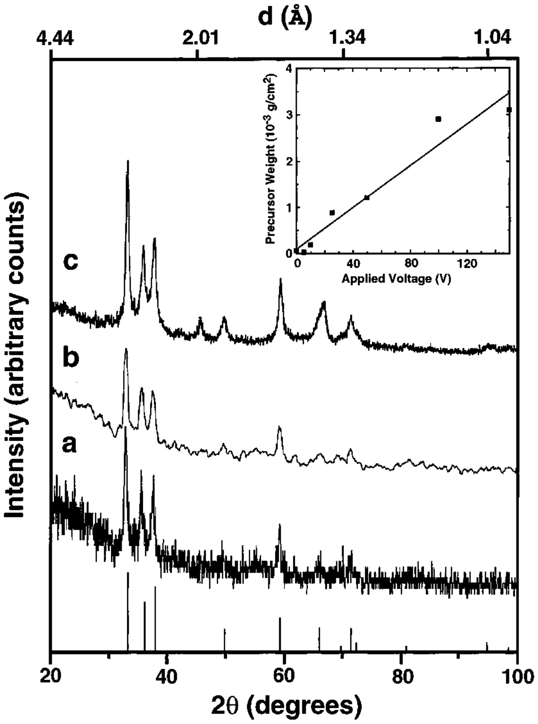

Figure 2. Grazing-angle XRD spectra of an n-Si cathode coated with AlN: (a) the raw data; (b) the same raw data after the application of a 25-point smoothing routine; (c) a conventional XRD spectrum of AlN scraped from the cathode. The JCPDS file-card pattern for AlN is shown at the bottom of the figure.[27] The inset is a plot of the weight of AlN precursor deposited vs the voltage used for the electrophoretic deposition. The deposition times were 1 min.

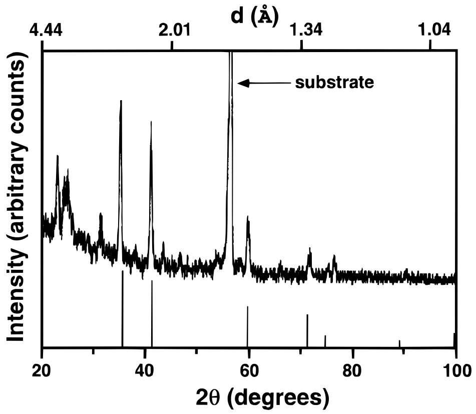

Figure 3. XRD spectrum of an n-Si cathode coated with δ-NbN. The diffraction peak indicated with an arrow is due to the n-Si substrate. The JCPDS file-card pattern for δ-NbN is shown at the bottom of the figure.[27] The slight offset of the diffraction maxima, compared to the JCPDS file-card pattern, is due to sample displacement caused by the finite thickness of the n-Si substrate.

the applied potential for 1 min depositions. At cell voltages below ~10 V we observe little or no deposition, but above this threshold the weight of precursor deposited is proportional to the applied potential in accordance with the Hamaker theory of electrophoretic yield.[17,18] The thick precursor coating formed at 150 V did not adhere well to the substrate when it was removed from the solution, so the deposition weight used for the plot in Figure 2 is somewhat low.

To further ensure that the applied potential is responsible for deposition, we positioned a n-Si substrate in the precursor/CH$_3$CN suspension next to the n-Si cathode during the 150 V deposition: no precursor deposited on this substrate. For short time-period depositions (<5 min) there were no visible signs of electrochemical reactions or electrophoretic deposition at the anode, but at longer times we observed pitting and a white coating, which we belive is AlBr$_3$ formed by slight dissolution of the anode in the Br-containing suspension.

An XRD spectrum of a n-Si cathode coated with NbN precursor[29] and calcined at 800 °C in Ar indicates that it is δ-NbN (Figure 3).[27] An XRD spectrum of an uncoated Si substrate, which had been calcined at 800 °C in Ar, shows that the peak indicated by the arrow is due to the (311) reflection of Si. Although the match between the JCPDS file-card spectrum for δ-NbN and the coating is very good, we are not able to identify the maxima at low 2θ (20−~33°). Interestingly, calcination of the precursor at 800 C in NH$_3$ results in γ-NbN (δ-NbN is the phase of NbN with the most desirable superconducting properties), which is consistent with

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[29] The precursor used for this experiment was the ammonolysis product obtained by dissolving NbBr$_5$ in liquid NH$_3$; it was not obtained by electrolysis of Nb in liquid NH$_3$/electrolyte solutions as the other two precursors were. The precursor is, nevertheless, a Br salt and cationic in CH$_3$CN, and our previous work indicates it is essentially identical with electrochemically prepared precursors (see refs 4, 24, and 25).

our earlier study of electrochemically prepared NbN powders.[4]

Ni_3N decomposes at temperatures above 400 °C, which is below the sublimation temperature of NH_4Br.[30] Therefore, we prepared the Ni_3N ceramic precursor in a 0.2 M NH_4Cl electrolyte solution, since Ni−Cl compounds resulting from the electrolysis of Ni electrodes in NH_4Cl/liquid NH_3 solution have lower sublimation temperatures than the Ni−Br compounds present in the AlN and NbN precursors. The single-phase Ni_3N coating was prepared by calcination at 375 °C in flowing NH_3. Figure 4 is the XRD spectrum of an electrophoretically prepared Ni_3N coating on n-Si, and it compares favorably with the card-file pattern shown at the bottom of the figure.[27]

Conclusion

Prior to the work reported here, we showed that electrochemical dissolution of Al, Nb, and Ni metals in liquid NH_3 leads to a metal nitride precursor, which can be calcined to form the corresponding ceramic material.[1−4,30] Here we have shown that the precursor can be electrophoretically deposited and subsequently calcined to yield metal nitride coatings. Electrophoretic deposition has some distinct advantages compared to techniques such as chemical or physical vapor deposition, or reactive sputtering. For example, it is technologically simple, well-suited for coating irregularly shaped, conductive objects, and it is amenable to the formation of complex layered and heterogeneous coatings.

Although the coatings obtained by this method are presently of poor quality, we believe optimization of the electrophoretic and calcination procedures will yield better films. For example, the high percentage weight loss of the coatings during calcination results in their rough texture, but vacuum heating prior to electrophoresis should remove volatile components of the precursor and lead to better films. We have not thoroughly characterized the precursor composition or structure, but these properties undoubtedly affect the structure of the metal nitride coating. More effective grinding or ball milling of the precursor powder, will yield smaller and more homogeneous particle sizes and should improve the coating density, homogeneity, and flatness. Finally, the deposition potential for the electrophoretic deposits could play a critical role in the density and morphology of the metal nitride ceramic products.

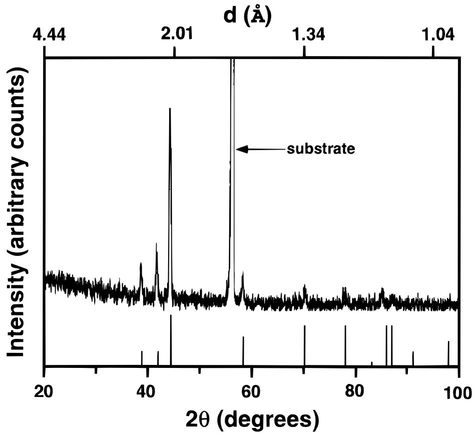

Figure 4. XRD spectrum of an n-Si cathode coated with Ni_3N. The diffraction peak indicated with an arrow is due to the n-Si substrate. The JCPDS file-card pattern for Ni_3N is shown at the bottom of the figure.[27] The slight offset of the diffraction maxima, compared to the JCPDS file-card pattern, is due to sample displacement caused by the finite thickness of the n-Si substrate.

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