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Preparation of monolithic AlN and composite TiN–AlN powders and films from precursors synthesized by electrolysis

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Abstract

Aluminum nitride (AlN) and TiAlN precursor solutions were synthesized by room temperature galvanostatic electrolysis of Al metal and Ti–Al alloy, respectively, in isopropyl-amine at a current density of 50 mA cm^{-2}. Monolithic AlN and composite TiAlN powders were prepared from these precursors by two-stage heat treatment at 400 °C in Ar and at 1200 °C in NH_3. Nitride films were produced by dip-coating and two-stage heat treatment of the precursor solution on silica glass substrates. The precursor solution used for the film preparation was concentrated from one-third to one-seventh by volume. The powders and films were characterized by XRD, chemical analysis, XPS and SEM/TEM observation in terms of phase evolution, particle size, film thickness and impurity content. The AlN and TiN–AlN films prepared from the concentrated precursor were smooth and flat, and were composed of uniform grains less than 100 nm in size.

Keywords: Electron microscopy; Film deposition; Infrared spectroscopy; Nitrides; Surface morphology; Thin films

1. Introduction

Aluminum nitride (AlN) exhibits useful properties, such as high thermal conductivity and high electrical resistivity [1] and is thus widely used as electronic substrates where high thermal conductivity is required and as protective coatings. On the other hand, (Ti, Al)N coatings have attracted much attention because of their improved oxidation resistance at elevated temperatures compared with monolithic TiN coatings and because of their improved performance in certain machining operations. AlN and (Ti, Al)N coatings are usually made by physical vapor deposition (PVD), such as sputtering [1,2], arc ion plating [3] or chemical vapor deposition (CVD) at higher temperatures (>1000 °C) using chloride ($TiCl_4$ and $AlCl_3$) vapor [4,5]. The author (S.S.) has reported the preparation of TiN, AlN and (Ti, Al)N films from alkoxide solutions at 600–800 °C by plasma-enhanced CVD [6–9].

Ti- and Al-amides have been used as precursors for the preparation of TiN and AlN powders or films, but their synthesis needs highly specialized synthetic skills in the techniques of organic chemistry. By comparison, electrochemical synthesis provides a simple, useful method for the preparation of the metal-organic precursors at room temperature, without the need for special apparatus or techniques. Electrolysis of Ti or Al in amine solution with a non-aqueous solvent makes it possible to synthesize the metal nitride precursors.

There have been a few reports on film preparation from precursors synthesized by electrolysis. Wade et al. produced AlN and NbN coatings on Si wafers by electrophoresis using electrochemically synthesized nitride precursors, but many cracks or agglomerated particles were formed on the film [10–12]. Russel and co-workers reported the preparation of TiN, AlN and (Al, Ti)N films by pyrolysis of precursors produced by electrolysis of Al and/or Ti electrodes and amine; these films were, however, not characterized [13–15]. The author (S.S.) reported the preparation of TiN powders and films from precursors synthesized by electrolysis of Ti and *n*-butylamine [16,17]. As in our previous study, it is interesting to produce AlN powders and films by the combined method of electrolysis and pyrolysis. It is also of value to produce coatings of (Ti, Al)N films with a fixed composition, using

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precursors synthesized by electrolysis of Ti–Al alloy with amine. This paper describes the synthesis of precursor solutions of AlN and (Ti, Al)N by electrolysis of Al and Ti–Al alloy and *i*-propylamine and the subsequent preparation of AlN and (Ti, Al)N powders and films by pyrolysis of the precursors in NH_3. The precursor solution used for the film preparation was concentrated from half to one-seventh by volume.

2. Experimental procedures

The experimental procedures for synthesis of AlN and (Ti,Al)N powders and films are shown in Fig. 1. A solution of acetonitrile (CH_3CN), isopropyl-amine, ($(CH_3)_2CHNH_2$) and tetrabutylammonium bromide (TBAB) solution was purified as reported elsewhere; TBAB was used as supporting electrolyte [17]. A mixed solution of $(CH_3)_2CHNH_2$ (10 ml) and TBAB (2 g) dissolved in CH_3CN (50 ml) was poured into an electrolytic cell in a three-necked flask, which was placed in a glove box in flowing argon. A polished Al or Ti–Al sheet (20 mm × 10 mm × 0.5 mm) was used as the anode and a platinum plate as the cathode. The Ti–Al sheet was obtained from a Ti–Al alloy produced by arc-melting of Ti and Al metal. Before use, the Al and Ti–Al sheets were cleaned with Na(OH) solution and distilled water and subsequently, with HNO_3 solution, ethanol and distilled water. Table 1 shows the crystalline phases in the alloy determined by XRD analysis. The major phases were $AlTi_3$/Ti and Al_3Ti/Al at the higher Ti and Al contents, respectively. Arc-melting of an Al/Ti = 6:4 composition formed an alloy of TiAl.

Galvanostatic electrolysis of Al and isopropyl-amine was carried out at a current density of 50 mA cm^{-2} at room temperature (Fig. 1), producing the precursor solution, which solidified after drying at 200 °C in vacuum. The weight change of this solid on heating at a rate of 10 °C min^{-1} up to 1200 °C in argon was monitored by thermogravimetry (TG). The solid was nitrided by a two-stage heat treatment at 400 °C in Ar and at 1200 °C in flowing NH_3. The precursor and nitride solids were characterized by XRD analysis and FT-IR. The carbon, nitrogen and hydrogen contents in the AlN precursors were determined by chemical analysis based on

Table 1
Phases in alloys determined by XRD

Al/Ti	Phases
8/2	Al_3Ti, Al
6/4	AlTi
4/6	$AlTi_3$
2/8	$AlTi_3$, Ti

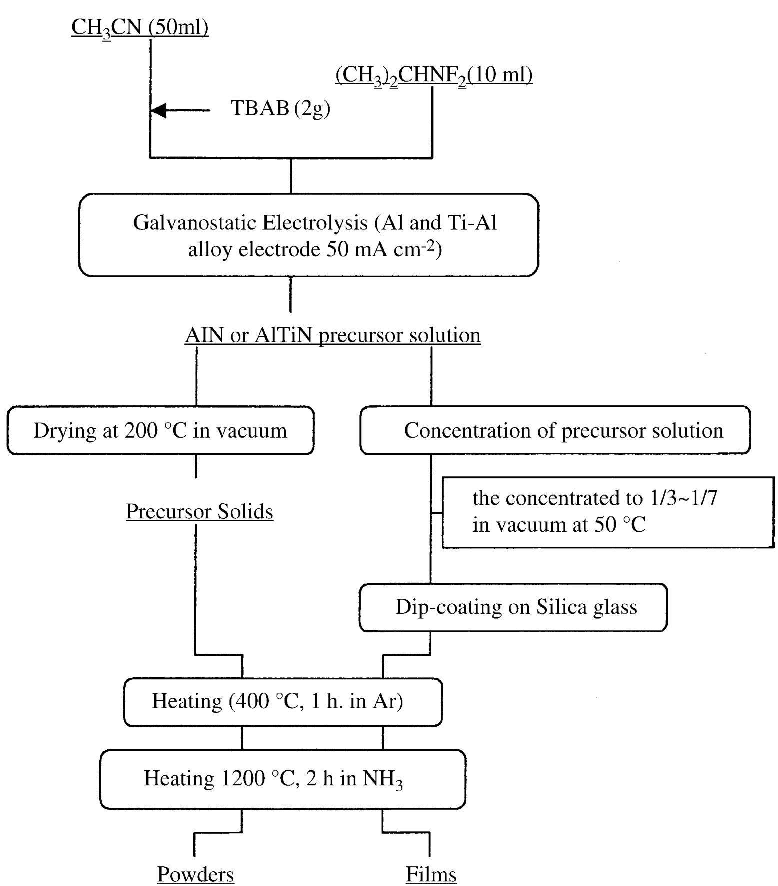

Fig. 1. Flow chart for experimental procedure.