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Synthesis of anticorrosion SiC and SiN_x films from alkoxide solution using liquid injection PECVD

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Abstract

Monolithic SiC, SiN_x and their duplex SiC–SiN_x films were synthesized from hexamethyldisiloxane solution at 750 °C on Si wafer and SUS304 steel substrates using $Ar/H_2/N_2$ plasma enhanced chemical vapor deposition (PECVD). The films were characterized by scanning/transmission electron microscopy (SEM/TEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). Amorphous SiN_x films were easily deposited on two kinds of substrates from thermal $Ar/H_2/N_2$ plasma, whereas crystalline SiC films synthesized using thermal Ar/H_2 plasma was only achieved on Si substrate and severe etching of the steel substrate by the plasma was observed. By varying N_2 flow rate from 4.5 l/min to zero at the intermediate period of the deposition process, a duplex SiC–SiN_x film, consisting of a top SiC and an inner SiN_x layer adjacent to the substrate, was obtained both on Si and steel substrates. The corrosive exposure test in KCl atmosphere at 650 °C indicated that the ceramic film-coated steel substrates demonstrated a much superior corrosion resistance in comparison with the uncoated one.

Keywords: SiC; SiN_x; Plasma CVD; Alkoxide solution; Protective coating; Corrosion resistance

1. Introduction

Both silicon nitride and silicon carbide have excellent mechanical and chemical properties such as high hardness, strength and thermal/chemical stability as well as good dielectric properties. They have wide applications ranging from protective coatings against wear, erosion–corrosion to microelectronic devices, X-ray mask materials and antireflection coatings [1–5]. The films or coatings are commonly produced by PVD or thermal CVD and, in particular, by a plasma enhanced deposition process allowing high deposition rates at lowered substrate temperatures [6,7]. Silicon nitride and carbide films can be synthesized from a variety of silicon sources, typically using silane or silicon-halogens ($SiCl_4$, CH_3SiCl_3, Si_2Cl_6) as the precursor and nitrogen or ammonia as the reactive gas [8–11]. However, silane is explosive and poisonous, and the halogen-containing precursors cause environmental problems and their residual impurities also deteriorate the film properties. Although organosilane compounds like hexamethyldisilazane are useful sources, they are relatively expensive [12].

Recently, a series of ceramic films have been synthesized by a liquid injection PECVD method using metal alkoxide solutions as the raw sources [13]. Such precursors have advantages of low cost, convenient storage and easy to handle. In this paper, we try to produce SiC and SiN_x films from the same Hexamethyldisiloxane ($((CH_3)_3SiOSi(CH_3)_3)$, HMDS) precursor in different plasma gas mixtures. Furthermore, these two films were deposited onto SUS stainless steel substrate to examine their feasibility as protective coatings for steels in a KCl vapor atmosphere. The results showed that SiN_x film could be directly deposited onto Si and steel substrates, but a direct deposition of SiC on steel substrate was not successful. This obstacle was solved by developing a SiC–SiN_x duplex film in which SiN_x acted as an intermediate layer to enhance the adhesion strength of SiC

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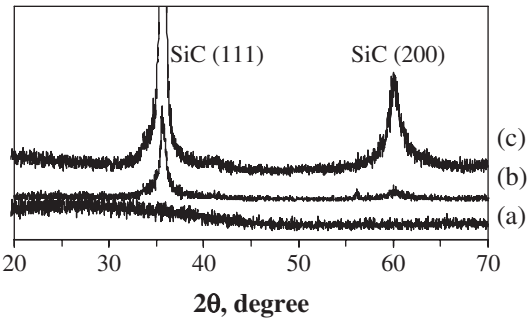

Fig. 1. XRD patterns of SiN_x (a), SiC–SiN_x (b) and SiC (c) films deposited on Si wafer.

to the steel substrate. Enhanced corrosion resistance on the steel substrates by imposing these ceramic films was achieved.

2. Experimental

The deposition process was performed at a conventional induction coupled thermal plasma apparatus (JHS-15M, JEOL). It is equipped with a torch, a solution feed system, a water-cooled chamber, and a vacuum system [13]. A 4 MHz r. f. coil provides a maximum power supply of 15 kW. The HMDS solution was premixed with dry ethanol solvent at a molar ratio of 1:1.7. The chamber was initially evacuated to a pressure of 1 Torr then the gases were introduced. An $Ar/N_2/H_2$ mixture was used as the outer tangential gas and Ar as the inner tangential gas passing through the torch head nozzles to produce plasma and spray the alkoxide solution into the plasma flame. The plasma was ignited at a plate voltage of 7.8 kV and a plate current of 2.7 A, while the deposition pressure was stabilized at 300 Torr. Using a high pressure liquid chromatography pump, the mixed solutions were injected at a feed rate of 0.05 ml min^{-1} for 15 min into a thermal Ar/H_2 plasma for SiC film and $Ar/H_2/N_2$ plasma for SiN_x film preparation, respectively. The duplex SiC–SiN_x films were prepared by feeding the HMDS solution into $Ar/H_2/N_2$ plasma for the initial 10 min to produce a SiN_x inner layer, then nitrogen was stopped abruptly and the deposition was continued in Ar/H_2 plasma for another 10 min to obtain a SiC top layer. The substrates were (100) Si wafer and SUS304 stainless steel (Fe–18Cr–8Ni) with dimensions of $10\times10\times1$ mm^3. These substrates were subjected to a deposition temperature of about 750 °C, which is measured by a thermocouple mounted beneath the stainless steel substrate holder. The flow rates of H_2 and N_2 were controlled by flow-meters at 1 and 4.5 l/min, respectively. The Ar gas used as outer and inner tangential corresponded to 2.5 and 8 l/min. Corrosion resistance of the ceramic film-coated SUS substrates was compared with the uncoated one by exposing them in an air-KCl vapor atmosphere at 650 °C for 48 h [14,15]. The phase identification, composition and chemical states analysis, morphological observation of the films were conducted by thin film X-ray diffraction, X-ray photoelectron spectroscopy, scanning and transmission electron microscope, respectively.

3. Results and discussion

Fig. 1 shows XRD patterns of the deposited films on Si wafer. No diffraction peaks are observed on SiN_x film (Fig. 1a) whereas SiC films grown on Si wafer (c) or on the SiN_x intermediate layer (b) exhibit sharp crystalline peaks. In addition, stronger diffraction peak intensity exists on the SiC films grown on Si wafer than that on the SiC–SiN_x system. This difference could be caused by the different crystallinity and purity of the films. For instance, the SiC film formed on Si wafer has a relatively pure composition, whereas the SiC film grown on SiN_x intermediate layer contains an additional 10 at.% bonded nitrogen, which can remarkably affect the orientation of the crystalline SiC. The SiN_x film formed on Si wafer exhibits typical cauliflower morphology on the surface (Fig. 2a). XPS analysis of this film demonstrates a Si_{2p} main peak at a binding energy of 101.7 eV, corresponding to Si–N bond. TEM observation in combination with SAED confirms the formation of amorphous phase in the film (Fig. 2b). The oxygen and free carbon that remained in the film are around

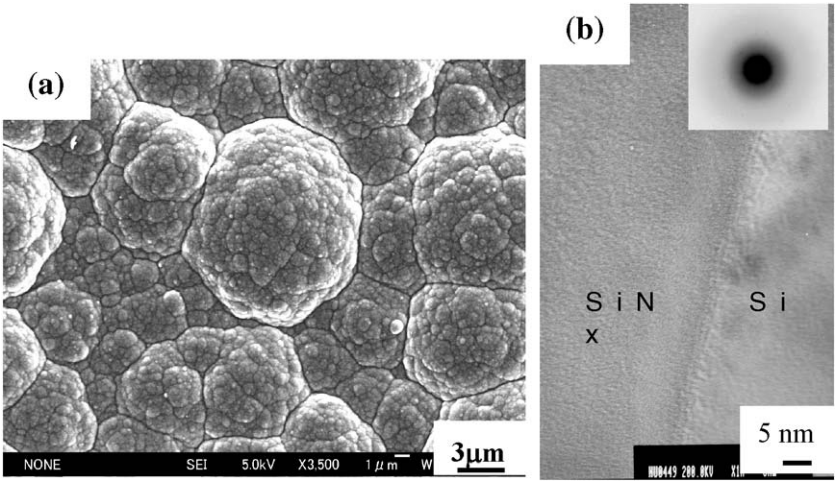

Fig. 2. SEM surface morphology (a) and TEM cross-sectional image (b) with inset SAED pattern of SiN_x film deposited on Si wafer.