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Multifunctional Silicon Aluminum Oxynitride (SiAlON) Ceramic Coatings for High Temperature Applications

Project Period: June 1, 2002 to May 30, 2005

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1. Executive Summary

This project has demonstrated how controlled synthesis of nanostructured SiAlON thin films with varying composition produces an outstanding class of wear resistant and oxidation resistant coatings. SiAlON thin films spanning the full range of O/N and Al/Si ratios were deposited by RF magnetron co-sputtering of Al and Si targets in Ar/O₂/N₂ mixtures onto bare sapphire and Pt coated sapphire substrates. The films are amorphous and very smooth when deposited at 200°C and remain amorphous even after extended post-deposition annealing in vacuum, N₂, or air up to 1500°C. Nitrogen rich film compositions are extremely wear resistant when measured in sliding contact with steel or sapphire pins. The film stoichiometry remains unchanged at high temperature in vacuum or N₂ but the films lose nitrogen during air annealing. A thin film interfacial oxidation sensor was developed and embedded at the SiAlON / substrate interface, and the oxygen penetration rate through the SiAlON film structures was inferred during isothermal annealing experiments at 1000°C in air. Film exposure to O* and O₂* species produced by an electron cyclotron resonance (ECR) source leads to rapid surface oxidation and nitrogen loss. Gradient film compositions offer the possibility of improved oxidation resistance.

1.1 Need for and Applications of SiAlON Thin Film Coatings

A critical need exists to develop new tough, oxidation resistant, and wear resistant ceramic coatings that can operate in high temperature (1000-1500°C) hostile environments.¹ Example applications for these protective coatings include aeronautic and aerospace components, turbine engines and cuttings tools.^{2,3} In these applications, the ceramic coatings must exhibit excellent heat resistance, chemical stability, fracture toughness and wear durability. Unfortunately, current high temperature ceramic coatings such as alumina, zirconia, or silicon nitride suffer from cracking, delamination, and chemical degradation upon thermal cycling in reactive environments that are routinely encountered in service. Thin film silicon aluminum oxynitride (SiAlON) coatings offer the potential of satisfying these performance demands.

Sintered SiAlON bulk ceramics have received considerable attention since their initial development in the 1970's⁴. Depending on synthesis conditions, crystalline or glassy ceramic phases can be produced which have useful thermal, chemical, and mechanical properties. SiAlON materials are essentially an alloy of aluminum oxide and silicon nitride. Alternatively, they can be viewed as aluminosilicates in which oxygen anions are partly replaced by nitrogen. By combining both oxide and nitride properties into bulk sintered SiAlON ceramics, the result is improved hardness and fracture toughness as shown in Figure 1.

While SiAlON's have been studied extensively in bulk form,⁵ very few studies have been carried out on thin films (< 1 µm thick) that are carefully prepared by controlling film growth at the atomic level. Thick (>100 µm) SiAlON ceramic coatings grown by CVD have been commercialized⁶ as an ultra-hard coating replacement for Si₃N₄, for potential applications in machine tools, bearings, turbochargers, engine valves and other components requiring high wear resistance. The β'-SiAlON composition (see Section 3.1) has been emphasized, and while it exhibits desirable hardness and wear properties, it also has been reported to be unsuitable for

¹ N.P. Padture, M. Gell, E.H. Jordan, Science 296 (2002) 280

² R.J. Brook (editor), *Advanced Ceramic Materials*, Cambridge, MA: MIT Press (1991)

³ H. Kaya, Comp.Sci.Tech. 59 (1999) 861

⁴ K.H. Jack, J. Mater. Sci. 11 (1976) 1135

⁵ *Proceedings of the International Symposium on SiAlONs*, Ed. K. Komeya, M. Mitomo, Y.B. Cheng (Trans Tech Publications LTD, Switzerland, 2003)

⁶ Kennametal Inc., Latrobe, PA; www.kennametal.com

"demanding applications".^{7,8,9} Our approach of synthesizing nanostructured SiAlON coatings via physical vapor deposition (PVD) methods appears to be a means to control defect microstructure and achieve enhanced performance.

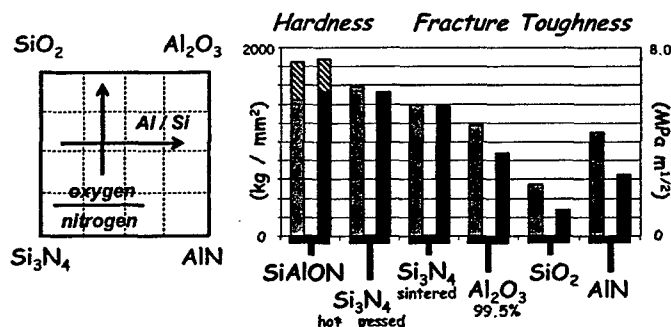


Figure 1 (a) Composition diagram showing stoichiometry ranges in SiAlON materials. (b) Comparison of hardness and fracture toughness of several bulk ceramics as reported in references^{10,11}. The cross hatches indicate ranges of values for SiAlONs as dictated by exact stoichiometry.

1.2 Major Research Accomplishments from this Project

Our results demonstrate that amorphous SiAlON films deposited by RF magnetron sputtering are very promising candidate materials for many current and future aeronautic and aerospace technologies that involve high temperature structural and propulsion materials. We also demonstrate that an oxidation sensor embedded in the SiAlON coating provides a very useful means for *in situ* evaluation during testing in high temperature environments.

The following list summarizes the major findings / accomplishments during the funding period.

- Conditions were established to synthesize homogeneous SiAlON films (up to 2 μm thick) with precise stoichiometry control using RF magnetron sputtering of Al and Si targets in Ar/N₂/O₂ mixtures.
- SiAlON films have amorphous structure as determined by electron and x-ray diffraction, and the glassy structure persists even after annealing in air at 1500°C for 10 days.
- The SiAlON films are completely miscible over their entire stoichiometry range and do not phase separate. X-ray photoelectron and Auger analysis indicates preferential formation of local Al-O and Si-N bonds which presumably stabilizes the amorphous structure.
- The glassy SiAlON films are extremely smooth, having a typical roughness of < 3 nm for a 1 μm thick film over a 100 μm^2 area.
- SiAlON films with the β' composition (Si_{6-z}Al₂O_zN_{8-z} with 0 < z < 4) are extremely wear resistant as indicated by significant wear of sapphire and steel pins and no film wear track in pin-on-disk tests; films with higher oxygen content show wear tracks in addition to pin wear.

⁷ H. Zhang, X. Zhong, "Synthesis of β -SiAlON by Reaction Sintering", Am. Ceramic Soc. Bull. (Aug 2002) 9701-9705

⁸ W. Schnick, "Nitridosilicates, oxonitridosilicates (sions) and oxonitridosilicates (sialons) New materials with promising properties", International Journal of Inorganic Materials 3 (2001) 1267-1272

⁹ A. Rosenflanz, "Silicon nitride and sialon ceramics", Current Opinion Solid State & Mater. Sci. 4 (1999) 453-459

¹⁰ Accuratus Corporation, <http://www accuratus.com/materials.html>

¹¹ Ferro-Ceramic Grinding, Inc., <http://65.108.128.37/ceramic-properties.php>

- Annealing SiAlON films in air above 1000°C or exposing them to O* radicals from an ECR plasma source causes surface oxidation; the film stoichiometry remains essentially unchanged by vacuum or N₂ annealing.
- An *in situ* interfacial oxidation sensor was developed and used to monitor the kinetics of oxygen penetration through the SiAlON films.
- Technology transfer activities include the following: (i) SiAlON films are being further evaluated as wear resistant passivation layers by two small Maine companies; (ii) thermal shock behavior is being measured in collaboration with RWTH Aachen, Germany; and (iii) high temperature pin-on-disk wear tests are being done at Air Force Research Laboratory.

2. SiAlON Thin Film Synthesis and Characterization

Several methods can be used to synthesize SiAlON ceramics. The easiest bulk method is to sinter mixtures of Si₃N₄-SiO₂-AlN and Al₂O₃ above 1500°C, but the uniformity and densification is difficult to control.^{12,13} An alternative method is to use a reduction and nitridation process of clay-carbon mixtures^{11,14} or silica-alumina gels.¹⁵ Kennametal Inc. (Latrobe, PA) has commercialized several SiAlON materials and thick film coatings.¹⁶ While synthesis methods of bulk SiAlON materials are well developed, very little work has been done in the area of SiAlON thin film synthesis. Bodart et al. used ion implantation of oxygen and nitrogen into sputtered Si_xAl_y coatings to create homogenous SiAlON coating layers.^{17,18,19} DC and RF sputter deposition of SiAlON thin films have also been reported,^{20,21,22} but minimal characterization was performed on these films. In this research project, we have established conditions for precise deposition of SiAlON films (10 nm to 2 μm thick) and have characterized their local chemical bonding, wear resistance, and high temperature oxidation rate.

2.1 Nanostructured Thin Film Architecture

Several different strategies for manipulating the film architecture were explored, as shown in Figure 2, including homogeneous films, multilayer films with various repeat spacings, films with

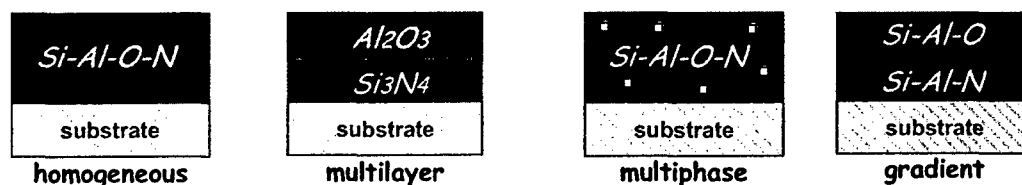


Figure 2 Several strategies for fabricating SiAlON films with nanostructured architecture.

¹² K. Watari, S. Sakaguchi, S. Kanzaki, T. Hamasaki, and K. Ishizaki, J. Mater. Res. **9** (1994) 2741

¹³ A. Seron, F. Beguin and J. Thebault, J. Mater. Res. **9** (1994) 2079

¹⁴ F.J. Narciso, A. Linares-Solano, and F. Rodriguez-Reinoso, J. Mater. Res. **10** (1995) 727

¹⁵ P.D. Ramesh and K.J. Rao, J. Mater. Res. **9** (1994) 1929

¹⁶ SiAlON Materials Development at Kennametal Inc. http://web.ornl.gov/sci/de_materials/documents/Yeckley.pdf

¹⁷ M. Jacobs, F. Bodart, G. Terwagne, D. Schryvers, A. Poulet, Nucl. Instruments in Phys. Res. B **147** (1999) 231

¹⁸ M. Jacobs and R. Bodart, Surf. and Coatings Tech. **103-104** (1998) 113

¹⁹ F. Bodart and M. Jacobs, Nucl. Instruments in Phys. Res. B **118** (1996) 714

²⁰ M. Jacobs, G. Terwagne, Ph. Rodquiny, F. Bodart, "Unbalanced magnetron sputtered Si-Al coatings: plasma conditions and film properties versus sample bias voltage", Surf. Coatings Technol. **116-119** (1999), 735-741

²¹ O. Soichi, Y. Suzuki, M. Yoshitake, K. Natsukawa, "Silicon-Aluminum Oxynitride composite films deposited by reactive ion beam sputtering", IEEE Proceedings (1999)

²² O. Knotek, F. Löffler, W. Beele, "PVD coatings in the system SiAlON", Key Engineering Mater. **89-91** (2002) 275

second phase precipitates, and films with gradient composition. Most of our effort was focused on homogeneous and gradient films. The film thicknesses used in the studies ranged from 10 nm through 2 μm . The use of these different nanostructures offers the possibility of controlling residual stresses, film adhesion, and the relative degree of crystalline/amorphous structure.

2.2 Accurate Stoichiometry Control by RF Magnetron Sputtering

Several different methods were used to deposit the SiAlON films including RF magnetron sputtering with SiAlON, AlN, SiO₂, Si, and Al targets in Ar/N₂/O₂ gas mixtures. It was found that the SiAlON sputter target acquired from Mitsubishi Materials Corp. contained a large Fe contamination (~2 at.%); such contamination was subsequently verified by Mitsubishi upon tests in their laboratory. The use of the SiAlON and other multi-component targets such as AlN and SiO₂ also had a major problem of target aging leading to irreproducible film compositions over time. Co-sputtering of elemental Si and Al targets in 50% Ar + 50% N₂/O₂ gas mixtures (Figure 3) yielded the necessary control to achieve highly reproducible depositions, and hence it was the method we focused on in our studies. It is also important to use a NuPure[®] N₂ filter on the N₂ source bottle,²³ especially when depositing nitrogen-rich films, to maintain the necessary gas purity (i.e. low oxygen contamination).

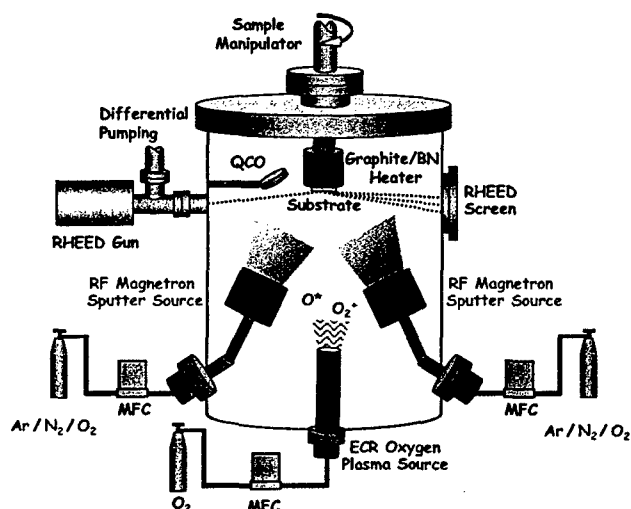


Figure 3 Synthesis of SiAlON films via RF magnetron co-sputtering of Al and Si targets in Ar/O₂/N₂ mixtures onto bare sapphire and Pt coated sapphire substrates.

Stoichiometry control was achieved by carefully monitoring the Al and Si fluxes during deposition using a quartz crystal oscillator (QCO) and adjusting the N₂/O₂ gas ratio using mass flow controllers. The important control parameters included the N₂/O₂ gas flows, total gas pressure, RF magnetron power, deposition rate, film thickness, and substrate temperature.

2.3 Film Synthesis and Processing Procedures

The SiAlON films were deposited on either bare or Pt-coated sapphire ($\alpha\text{-Al}_2\text{O}_3$) substrates that had the (01 $\bar{1}2$) r-cut plane orientation. The bare sapphire substrates were cleaned prior to SiAlON deposition by exposing them to an ECR oxygen plasma at 10⁻⁴ torr O₂ for 20 min

²³NuPure Corp. www.nupure.com

followed by annealing at 600°C in 10^{-4} torr O_2 for 30 min. This procedure produced a sharp RHEED pattern with well-resolved Kikuchi lines and a 1×1 LEED pattern indicating excellent surface order as shown in Figure 4. We also found that annealing the sapphire substrates at 1200°C in air for >24 hrs using a tube furnace yielded well defined step-terrace structures as observed by atomic force microscopy (Fig.4c); the influence of sapphire surface ordering and step bunching effects on subsequent film growth is currently being investigated in more detail in our lab. For some film depositions, the sapphire was coated with a 50nm layer of Pt over a 10nm adhesion layer of Zr using e-beam evaporation. This Pt layer was effective in reducing charging effects during the XPS measurements.

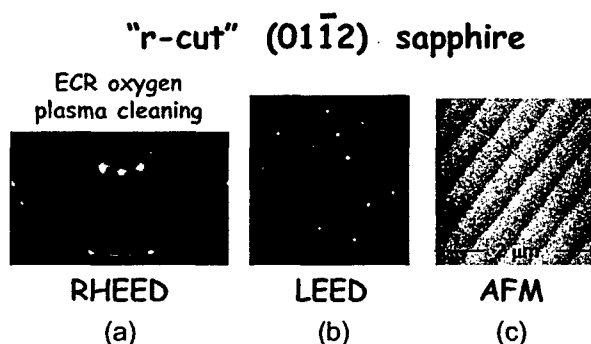


Figure 4 Characterization of a sapphire substrate surface prior to SiAlON film deposition. (a) 30kV RHEED pattern along the $[2\bar{1}\bar{1}0]$ azimuth (b) 130eV LEED pattern and (c) AFM image showing step-terrace structure.

SiAlON films spanning the full Al/Si and O/N composition ranges were synthesized by tuning the relative Si and Al fluxes through adjustment of the RF power to each sputter target and using a mixed 50% N_2/O_2 + 50% Ar plasma. Since the relative sticking/reactivity of oxygen versus nitrogen plasma species is very large, it was found that N_2/O_2 ratios between 92:8 and 99:1 were sufficient to yield SiAlON compositions over the entire O/N range. The exact film stoichiometries were achieved through control of RF power to the Al/Si sputter sources and very slight adjustments to the N_2/O_2 flows. Figure 5 shows all of the homogeneous film compositions that were deposited in our studies as determined by XPS measurements. Each of these films was deposited to a thickness of 200 nm using a substrate temperature of 200°C; film thickness was verified using surface profilometer over a shadowed edge following deposition.

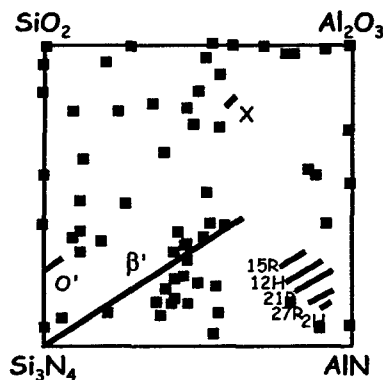


Figure 5 The homogenous SiAlON film compositions (green squares) synthesized in our studies as determined by XPS analysis.

2.4 Measurement of Chemical, Structural, and Mechanical Properties

In the Thin Film Synthesis, Processing and Characterization Facility at UMaine (Figure 6), the thin film deposition chamber is connected to several other ultra-high vacuum analysis chambers via a sample trolley transportation system. The analysis chambers provide capabilities for x-ray and ultra-violet photoelectron spectroscopy using a hemispherical analyzer (XPS and UPS), scanning Auger spectroscopy using a cylindrical mirror analyzer (AES), ion beam depth profiling with azimuthal sample rotation, low energy electron diffraction (LEED), variable temperature scanning tunneling microscopy (STM) / atomic force microscopy (AFM), and 4-point conductivity / Hall mobility characterization. This versatile apparatus allowed *in situ* measurements of the SiAlON film structure, composition, chemical bonding, and morphology to be carried out on as-deposited films as well as after thermal treatments in controlled atmospheres.

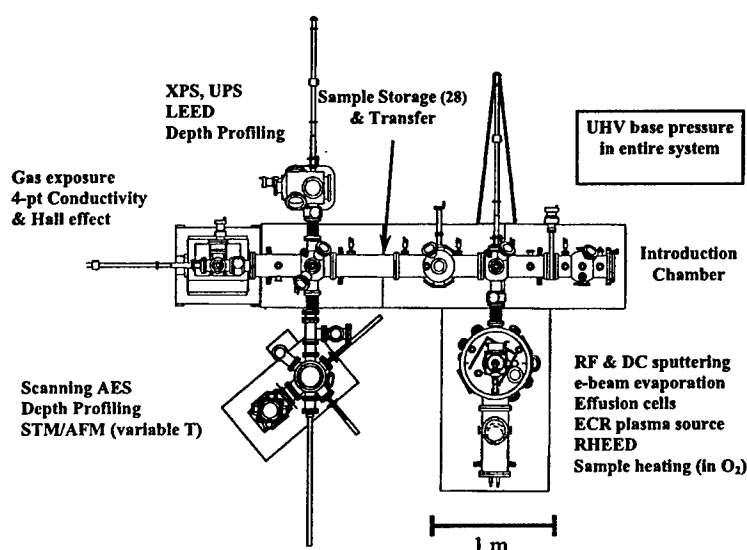


Figure 6 The Thin Film Synthesis, Processing, and Characterization Facility at UMaine used to perform *in situ* structural and chemical measurements on SiAlON films.

Post deposition treatments of the SiAlON films were carried out in vacuum, N₂, O₂, O[•]-radical, or air environments at temperatures between 25°-1500°C. *Ex situ* characterization included X-ray diffraction with a Scintag four-circle goniometer, and room temperature pin-on-disk wear measurements with variable loads and sapphire or steel pins. Wear tracks were measured using surface profilometry and atomic force microscopy. Chemical degradation of the films at high temperature was also monitored using an embedded interfacial oxidation sensor as discussed in Section 4.

3. Stoichiometry Effects and Chemical Bonding in SiAlON Films

3.1 Phase Diagram and Structure of SiAlON Ceramics

SiAlON materials are essentially an alloy of aluminum oxide and silicon nitride. Alternatively, they can be viewed as aluminosilicates in which oxygen anions are partly replaced by nitrogen. The fundamental structural building block consists of (Si,Al)(O,N)₄ tetrahedra. As a function of the (Si⁴⁺, N³⁻) vs. (Al³⁺, O²⁻) ratio, the bonding is expected to change from covalent to ionic

character. Figure 7 shows the phase diagram that has been reported for bulk SiAlON materials.²⁴ In this representation, the Si/Al ratio increases from left to right and the N/O ratio increases from top to bottom. Several phases are present that are iso-structural with several other more traditional ceramics. The β' -SiAlON phase is iso-structural with β - Si_3N_4 and hence has similar physical and mechanical properties, but because of its composition, its chemical properties approach those of alumina.²⁵ The β' range of composition can be written as $\text{Si}_{6-z}\text{Al}_2\text{O}_2\text{N}_{8-z}$ with $0 < z < 4$. The X phase has a composition of $\text{Si}_3\text{Al}_6\text{O}_{12}\text{N}_2$ and is iso-structural with the traditional refractory aluminum silicate material, 'mullite' ($\text{Al}_4.5\text{Si}_{1.5}\text{O}_{9.75}$). The O' phase is essentially a silicon oxynitride with composition $\text{Si}_{2-x}\text{Al}_x\text{O}_{1+x}\text{N}_{2-x}$ with $0 < x < 0.4$, being iso-structural with the orthorhombic $\text{Si}_2\text{N}_2\text{O}$ lattice. In the AlN rich corner of the diagram, there are several hexagonal and rhombohedral polytypes called Ramsdell phases that are modifications of the AlN wurtzite structure. In bulk SiAlON systems, each of these phases has been documented by X-ray diffraction analysis.²⁴

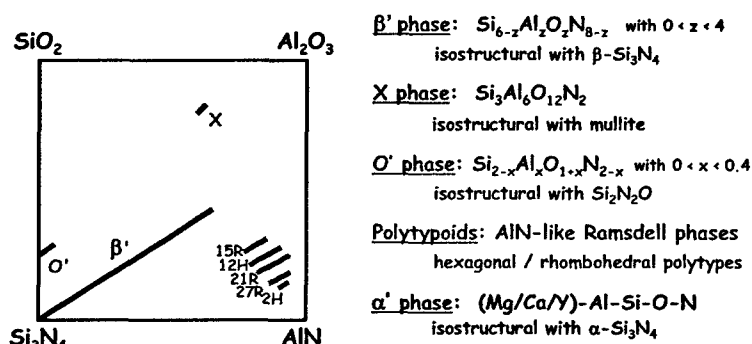


Figure 7 Phase diagram of the SiAlON system as reported by reference [24] showing several phases that are iso-structural with several other more traditional ceramics.

Another important SiAlON phase that does not appear on this equilibrium diagram is the α' phase which is formed by doping controlled amounts of multivalent ions into the SiAlON lattice. The α' -SiAlON structure is derived from α - Si_3N_4 by replacing some of the Si atoms by Al cations and accommodating additional metal cations such as Li, Mg, or Y in interstices for charge compensation. Much engineering development of the α' phase has been carried out because it has been shown to have outstanding toughness for application as cutting tools and in microturbine hot section components.²⁶

Glassy phases can also occur in the SiAlON system under certain processing conditions, particularly in metal doped systems. Electron microscopy has shown that nanometer thick glassy intergranular phases are present at most, but not all, grain boundaries in SiAlON's.²⁷ These intergranular phases, which appear to be a common feature in a wide range of silicon nitride, alumina, and zirconia ceramics, can provide high diffusivity paths for cations and can affect high temperature mechanical properties.²⁸

²⁴ K.H. Jack, J. Mater. Sci. 11 (1976) 1135

²⁵ K.H. Jack, in "Advanced Ceramic Materials," ed. by R.J. Brook (MIT Press, Cambridge, MA 1991) p. 411.

²⁶ G. Z. Cao, R. Metselar, "α-Sialon Ceramics: A Review", Chem. Mater., 3 (1991) 242-53; *Proceedings of the International Symposium on SiAlONs*, Ed. K. Komeya, M. Mitomo, Y.B. Cheng (Trans Tech Publications LTD, Switzerland, 2003)

²⁷ H. Schmid and M. Rühle, J. Mater. Sci. 19, 615 (1984).

²⁸ D.R. Clarke, in "Surfaces and Interfaces of Ceramic Materials," edited by L.C. DuFour, C. Monty, and G. Petot-Ervias (Klewer, Dordrecht, 1989) pp. 57-79.

A very important result that we found in our studies of the sputter deposited SiAlON films is that their structure is amorphous, as determined both RHEED and X-ray diffraction, both when deposited at 200°C and also after extended high temperature annealing up to 1500°C. RHEED analysis in the deposition chamber immediately following growth at 200°C showed completely diffuse patterns for all films, independent of composition. Numerous high temperature annealing experiments in vacuum, air, or nitrogen were carried out following deposition (see Sections 4 and 5). For every treatment, the films exhibited amorphous X-ray diffraction patterns. The amorphous structure persisted even after a 10 day anneal at 1500°C in a tube furnace. The amorphous nature appears to be a consequence of the local chemical bonding effects in these thin film materials.

3.2 XPS Analysis of Chemical Bonding Effects

X-ray photoelectron spectroscopy was performed in ultra-high vacuum on each of the homogeneous SiAlON films immediately after deposition and prior to any air exposure. Figure 8 shows an XPS spectrum acquired from a β' -SiAlON film with Mg K α x-rays. The core level peaks from O, N, Si, and Al are clearly seen as well as KLL type Auger transitions from each of the elements. (It should be noted that the Al and Si KLL transitions that occur at negative binding energy were excited by the bremsstrahlung x-rays and are correctly plotted in terms of kinetic energy in subsequent figures.) The intensities provide the information to carry out an accurate composition analysis and the exact binding energies reveal aspects of the chemical bonding. The XPS sampling depth is a function of the energy dependent inelastic mean free path, λ , and roughly 99% of the XPS signal arises from 3λ . Thus the depth in the SiAlON films over which the composition is analyzed ranges from ~6 nm for the N and O KLL emission to ~12 nm for the Al and Si KLL emission. This surface sensitivity is the reason why the XPS measurements must be done in ultra-high vacuum immediately after deposition in order to get a true value for film composition.

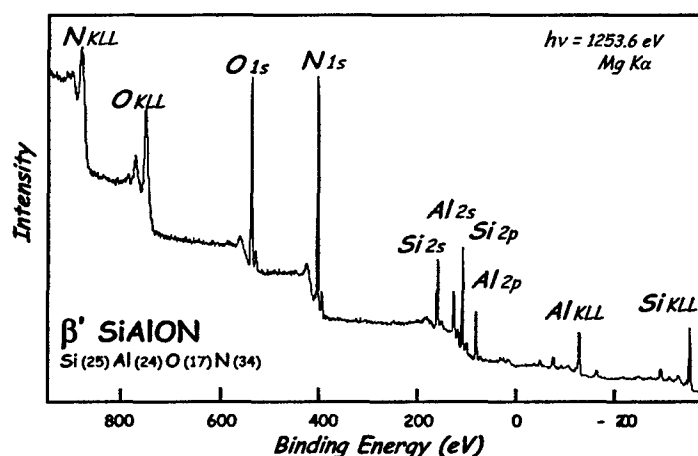


Figure 8 XPS spectrum from a β' composition SiAlON film acquired with Mg K α x-rays, showing both core level and Auger transitions.

Two sets of XPS experiments were done to probe the chemical bonding in the SiAlON films. These experiments focused on (i) a range of films with approximately equal Al:Si ratio and varying O:N ratio (Figure 9) and (ii) a range of films with approximately equal O:N ratio and varying Al:Si ratio (Figure 10). Because of steady state charging effects that occur during XPS

on insulating samples, the absolute binding energy scale is difficult to determine accurately. For the purpose of comparing the samples, all of the XPS data were corrected for charging (by typically ~6 eV) to align all spectra relative to an O1s peak at 530.1 eV, the reference energy used for pure aluminum oxide. This correction procedure allows very accurate relative binding energy shifts to be determined between samples.

As the Si:Al ratio in SiAlON films is changed (Figure 9) several important features can be discerned. The O KLL and N KLL lineshapes contain a principle peak and several additional peaks at higher kinetic energy which are related to the Auger transition fine structure; each of these smaller peaks are well known features in N and O Auger emission. The Si and Al core level emission also shows the expected lineshapes including plasmon loss features at ~20 eV higher binding energy. The important result that we find is that all the spectra line up at the same binding energies at all SiAlON compositions. This immediately indicates that the SiAlON films are homogenous and form a complete solid solution over the entire composition range. If phase separation and/or changes in local bonding had been present, these changes would have been easily discernable via binding energy shifts.

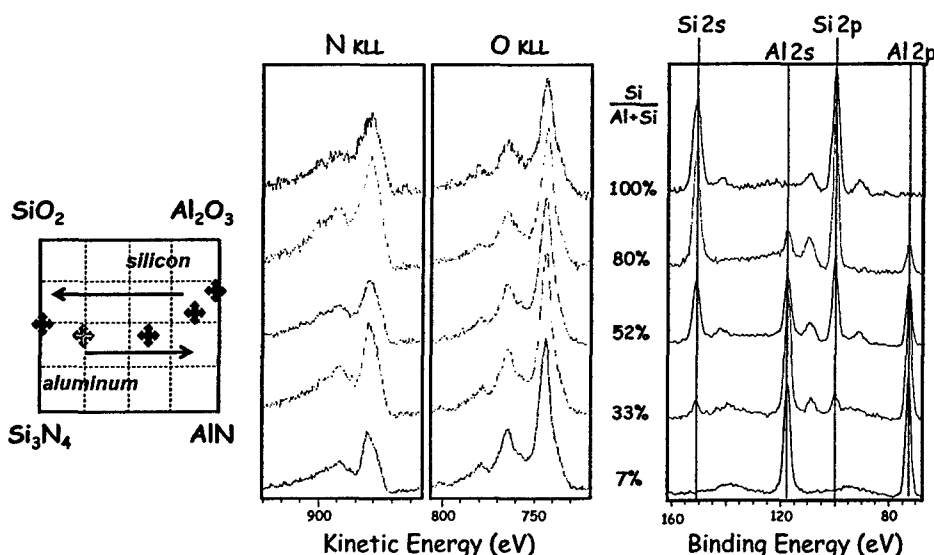


Figure 9 XPS Auger and core level spectra as a function of changing the Al:Si ratio in SiAlON films. The specific film compositions are indicated on the phase diagram.

The same result of complete solid solubility is generally followed as the O:N ratio in the SiAlON films is varied (Figure 10), except differences are observed as the film has a composition greater than a 80% O:N ratio. Up to 80% oxygen, there is an absence of any shift or peak shape change in the O1s or N1s lines or in the Al and Si KLL lines, including their fine structure, which again indicates solid solubility. At higher oxygen concentration, a new N1s peak emerges at approximately 5 eV higher binding energy than the main N1s line. This new emission feature is consistent with previous XPS studies of silicon oxynitride films²⁹ which show that the N1s emission is influenced primarily by nearest neighbor electronegative atoms. As the oxygen concentration gets large enough, many of the nitrogen atoms begin to have three oxygen nearest neighbors and these N-O bonds exhibit a large N1s shift to higher binding energy. The

²⁹ J. .P. Chang, M.L. Green, V.M. Donnelly, R.L. Opila, J. Eng, Jr., J. Sapeta, P.J. Silverman, B. Weir, H.C. Lu, T. Gustafsson, E. Garfunkel, J. Appl. Phys. 87 (2000) 4449; G.M. Rignanese, A. Pasquarello, J.C. Charlier, X. Gonze, R. Car, Phys. Rev. Lett. 79 (1997) 5174

main N1s line is still prevalent from nitrogen atoms also being bonding to neighboring Al and Si atoms. The other effect we observe as the SiAlON films becomes oxygen rich is that the Si emission shows a lower binding energy peak due to the formation of elemental Si⁰ instead of the Si⁴⁺ valence state; no reduced species are evident in the Al emission. This result suggests that the bond strength of Si-N and Si-O bonds are much weaker than the Al-N and Al-O bonds, and that some Si atoms may become reduced if there is a competition for available nitrogen or oxygen atoms. Subsequent processing of a film containing the Si⁰ feature, including annealing in vacuum at 1000°C, annealing in 10⁻⁵ torr O₂ at 800°C, exposure to air at room temperature, or exposure to an ECR oxygen plasma at room temperature did not have any noticeable influence on the Si⁰ peak. However, a 1000°C anneal in air caused the Si⁰ peak to disappear as oxygen species diffused into the film and oxidized all the Si atoms to the 4+ valence state (Section 4.1).

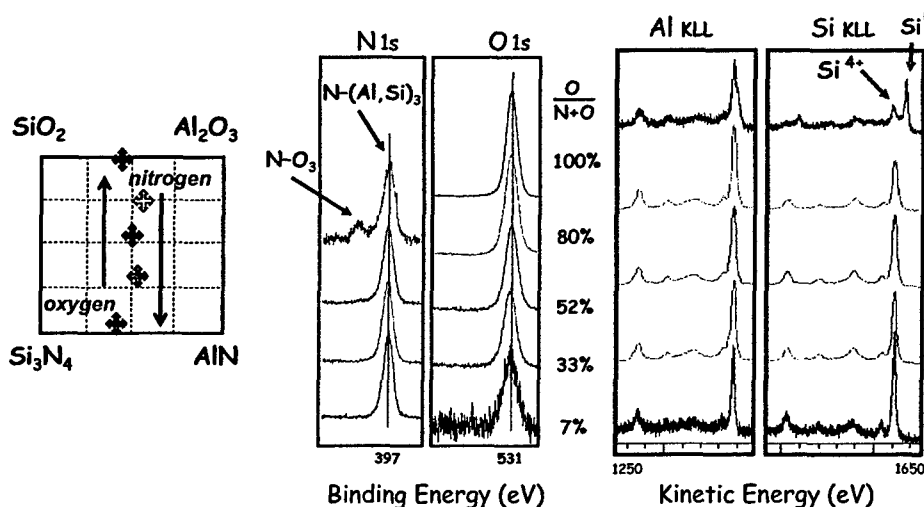


Figure 10 XPS Auger and core level spectra as a function of changing the O:N ratio in SiAlON films. The specific film compositions are indicated on the phase diagram.

Our XPS experimental results agree with recent theoretical calculations of chemical bonding and atomic ordering effects in β -SiAlON carried out by Okatov and Ivanovskii.^{30,31} They performed tight-binding band calculations using large atomic cells based on the β -Si₃N₄ lattice and considered energetics as a function of replacing some Al for Si and some O for N atoms in the structure. Figure 11 illustrates one such low energy configuration for a Si_{6-x}Al_xN_{8-x}O_x cell with x=3.

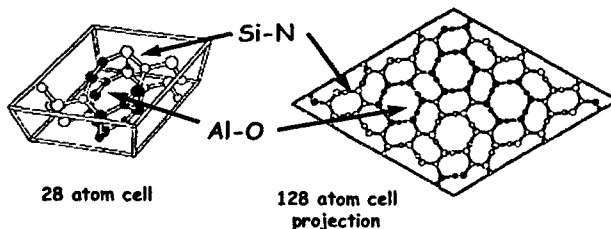


Figure 11 Models of the SiAlON structure used by Okatov and Ivanovskii³⁰ to calculate total band energy. (a) 28 atom supercell and (b) 126 atom supercell projected onto the (001) plane.

³⁰ S.V. Okatov and A.L. Ivanovskii, International Journal of Inorganic Materials 3 (2001) 923

³¹ S.V. Okatov and A.L. Ivanovskii, Phys. Stat. Sol. B 231 (2002) R11

Adding Al atoms into the Si_3N_4 lattice depopulates bonding states near the Fermi level and destabilizes the system. Likewise, O atom substitution causes antibonding states to become filled by the excess oxygen electrons, which also increases the system energy. However, if pairs of Al-O atoms are introduced, the bonding states are completely occupied and the antibonding states remain vacant. Hence, the total band energy is minimized when short-range atomic ordering occurs, with preference for Al-O bonds locally forming at the expense of Al-N and Si-O bonds. The driving force for local Al-O bond creation may explain why there is complete solid solubility as the SiAlON composition is varied, as observed in our XPS measurements. In addition, this bonding energetics explains the presence of the Si^0 state at high oxygen concentration since Al-O bonds are highly preferred.

3.3 Auger Parameter Analysis

'Auger parameter' measurements from the SiAlON films also reveal information about the local bonding characteristics. As established by Wagner *et al.*³², the modified Auger parameter, α' , defined as

$$\alpha' = KE (\text{Auger KLL}) - BE (\text{photoelectron } 2p)$$

where KE and BE refer to binding energy and kinetic energy, respectively, provides an accurate measure of the local bond polarizability in Al-O and Si-O compounds. A chemical state plot of KE versus BE yields a diagonal grid of α' values, with smaller α' values indicative of larger screening of the final state ion and hence a more ionic bond. Figure 12a shows polygon shaped regions in Auger parameter plots that represent the α' values that have been determined for a large number of Al-O, Al-N, Si-O, and Si-N compounds, as reported in an Auger parameter database.³² Our measurements of α' for SiAlON films as a function of nitrogen content are

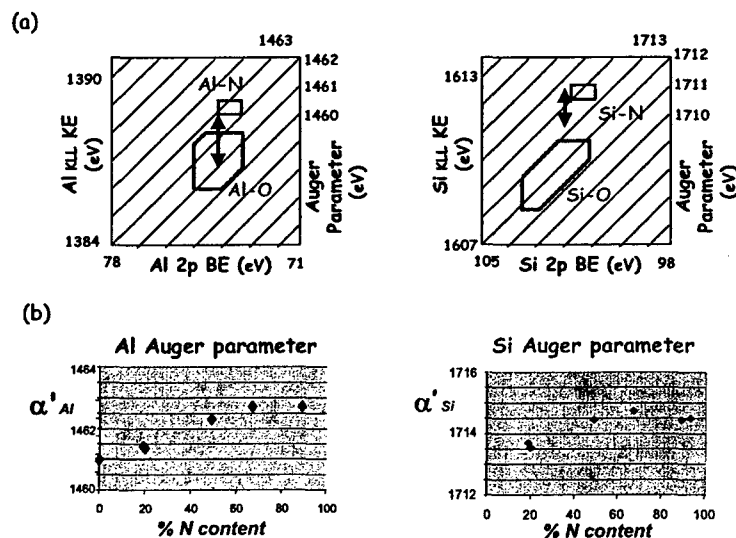


Figure 12 (a) Chemical state plots containing polygon shaped regions that show values of the Auger parameter for aluminum and silicon oxides and nitrides, as reported in reference 32. The arrows show ranges determined from SiAlON films. (b) Al and Si Auger parameters measured versus nitrogen content in SiAlON films.

³² C.D. Wagner, D.E. Passoja, H.F. Hillary, T.G. Kinisky, H.A. Six, W.T. Jansen, J.A. Taylor, J. Vac. Sci. Technol. 214 (1982) 933

shown as arrows in Figure 12a and plotted versus nitrogen content in Figure 12b. The very small spread of α' values for our SiAlON films is consistent with our XPS observations of complete solid solubility as a function of composition, as well as preference for Al-O and Si-N local bonding.

3.4 Wear Behavior versus Stoichiometry

Pin-on-disk wear testing at room temperature was conducted on SiAlON films with various stoichiometries to measure the film wear behavior. Each film was subjected sliding wear testing in contact with a steel or sapphire pin using normal loads from 1 to 80 grams; the contact radius was estimated to be $\sim 40 \mu\text{m}$. Following each test, the pin surface was examined with optical microscopy and the wear track was analyzed using surface profilometry. Figure 13 shows the results from two different N:O film compositions with approximately equal amounts of Al and Si, one with 90%N:10%O and the other with 30%N:70%O. For the nitrogen-rich film, the sapphire pin showed significant wear by optical microscopy and the SiAlON surface became covered by wear debris as measured by surface profilometry. However, there was no measurable wear of the SiAlON film until the load was increased to 80 grams. This is a significant result since sapphire has a hardness of 9 out of 10 on the Mohs hardness scale. The glassy structure and smooth surface of the film coupled with this extreme wear resistance suggests that these SiAlON films may be extremely useful as a room temperature protective layer on a variety of sensors and MEMS devices; further testing of this attribute is being explored in collaboration with several industrial partners (see Section 7).

The oxygen-rich SiAlON films were found to be less wear resistant. Wear tracks in the films became apparent at lower loads, although the sapphire pin also showed some wear. In this situation, the wear is governed by third body debris particles under the contact. As discussed in Section 4, these oxygen-rich films are more oxidation resistant above 1000°C than the nitrogen-rich films. Thus, the relevant measurements that need to be performed are pin-on-disk wear at elevated temperatures. These challenging experiments are just getting underway in collaboration with Dr. Andrey Voevodin in the Materials and Manufacturing Directorate at the Air Force Research Laboratory.

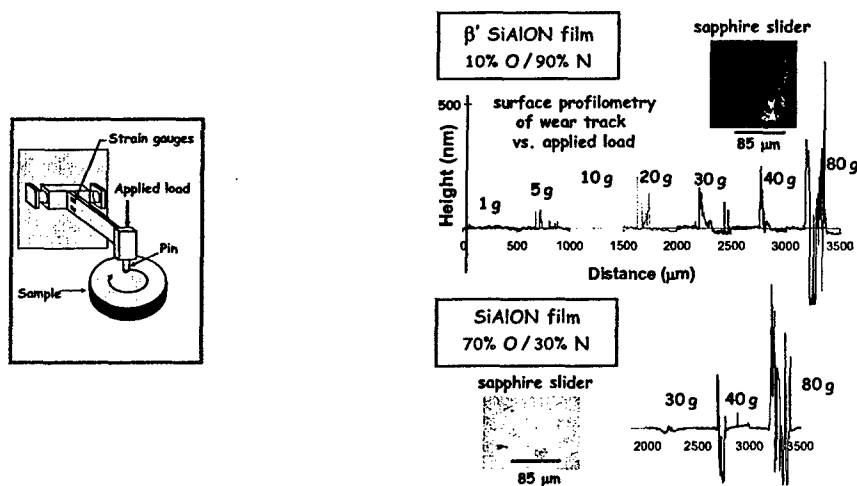


Figure 13 Pin-on-disk wear testing of a nitrogen-rich SiAlON film revealed debris build-up from wear of the sapphire pin and negligible film wear for loads below 80 g. The same test performed on an oxygen-rich SiAlON film showed wear of the film at much lower loads.

4. High Temperature Oxidation Behavior of SiAlON Films

4.1 Furnace Annealing Experiments in Air

An important aspect of this project was to evaluate the chemical degradation of SiAlON films in high temperature aggressive environments. SiAlON films with different compositions were subjected to post-deposition annealing in lab air at 1000°C in an alumina crucible placed in a tube furnace that was ramped to temperature at 10°C/min and held for several time intervals up to 10 days. Changes in surface stoichiometry were measured using x-ray photoelectron spectroscopy. Following air annealing at 1000°C for 2 hours (Figure 14), XPS showed that the nitrogen level in each the films was reduced to zero within the XPS sampling depth (~10 nm). X-ray diffraction also failed to show any evidence of crystalline structure even after air annealing treatments as long as 240 hours. The oxidation of the top surface is not surprising, and the more important question is what the rate of oxidation throughout the film is. This necessitated the use of a corrosion sensor located at the SiAlON film / substrate interface (Section 4.2).

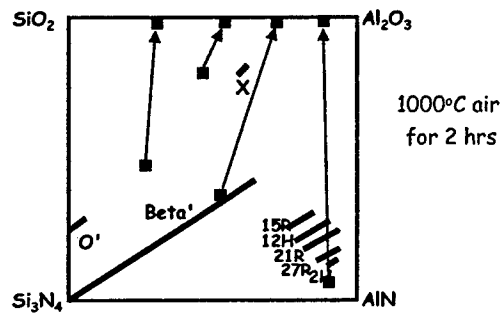


Figure 14 Changes in surface composition of several SiAlON films as measured by XPS following annealing at 1000°C in air for 2 hours.

Air annealing at 1000°C also eliminated the elemental Si⁰ XPS peak from oxygen rich SiAlON films that was present in the as-deposited films (see Section 3.2). Figure 15 shows the evolution of the Si XPS emission as a function of various surface treatments. The Si⁰ peak remains visible in the near surface region for all treatments except the 1000°C air anneal. This

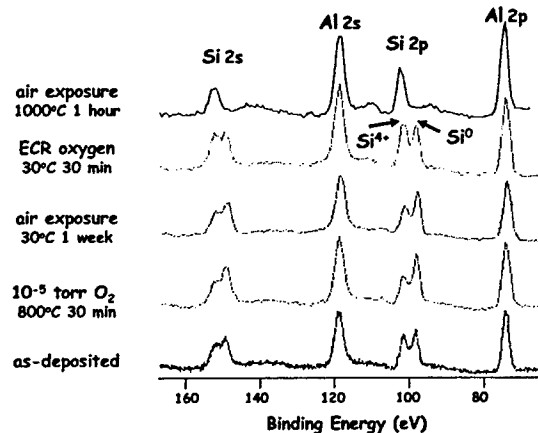


Figure 15 XPS spectra showing changes in the Si and Al emission as a function of different surface treatments.

result again supports the premise that Si atoms rather than Al atoms become reduced when there is a competition for N or O atoms. Only upon 1000°C air annealing does the Si⁰ peak disappear as oxygen diffuses into the film and oxidizes the Si atoms to the 4+ valence state.

4.2 Design and Construction of an Interfacial Oxidation Sensor

The SiAlON films were deposited on top of an 'interfacial oxidation sensor' that consisted of a photolithographic metal (Pt, Cr, or Ni-Cr) serpentine pattern on a sapphire substrate as shown in Figure 16. Changes in the resistance of this sensor were used to measure the rate of oxygen penetration through the SiAlON film. The use of different metals for the patterned structure yielded different oxidation kinetic parameters for the sensor as a means to characterize the oxygen penetration rate through the SiAlON film. The metal sensor was 250 nm thick and had the appropriate lateral dimensions to yield a starting resistance of nominally 100 Ω , and the change in resistance (up to 100 M Ω) was measured as the metal became oxidized during high temperature processing. The electrodes for wire bonding were fabricated from 60 nm thick Pt and included a 10 nm Zr layer to achieve reliable adhesion to the sapphire substrate.³³ The measurements were very tedious because of the poor reliability of wire bonds to the sensors. Often the bond wire connections deteriorated during the testing, which suggests the need for a more reliable microfabricated test platform in future studies.

The SiAlON covered sensors were ramped up in a tube furnace from ambient to 1000°C at a rate of 10°C per minute, and held isothermally for a specified numbers of hours while the sensor resistance was measured at 1 minute intervals for as long as 10 days.

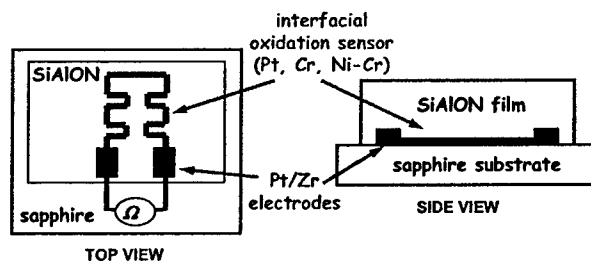


Figure 16 Patterned metal resistor (Pt, Cr, or Ni-Cr) at the SiAlON film / sapphire interface used to monitor chemical degradation at the interface via oxygen diffusion through the film.

An example of the resistance changes of two Ni-Cr interfacial sensors coated with two different thicknesses of β' SiAlON are shown in Figure 17a. The transitions in the resistance values are dependent on film thickness, but the interpretation of the resistance changes are complex as discussed in the next section. Figure 17b shows the oxidation behavior when using a pure Cr serpentine pattern as the sensor metal. The changes are much more continuous and the behavior is indicative of parabolic oxidation kinetics as discussed below.

4.3 Measurement of High Temperature Oxidation Rate Constants

The interpretation of the resistance changes of the interfacial oxidation sensor can be understood through a simple oxidation model. The oxidation reaction that occurs on the surface of the SiAlON film initially forms an oxide layer that creates a barrier that oxygen must diffuse through to react with the underlying SiAlON. The diffusion of oxygen occurs via Fick's first law

³³ G. Bernhardt, S. Silvestre, N. LeCursi, S.C. Moulzolf, D.J. Frankel, and R.J. Lad, *Sensors and Actuators B* 77 (2001) 368-372

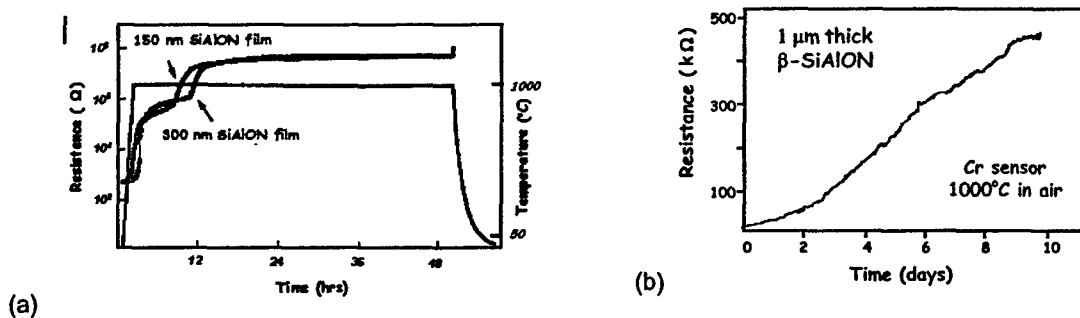


Figure 17 Resistance changes at 1000°C for (a) Ni-Cr sensors covered by β' SiAlON films of two different thicknesses and (b) 1 μm thick β' SiAlON film on a pure Cr sensor.

and is the rate limiting step for further oxidation. The patterned metal resistor (e.g. Cr) that makes up the oxidation sensor will oxidize at a rate that depends on the oxygen concentration available at the SiAlON / CrO_x interface; this in turn depends on the rate of oxygen flux through the SiAlON film. Figure 18 shows a basic model based on the popular Deal-Groves model for oxide growth kinetics³⁴ that defines the various oxygen concentrations. C_g is the oxygen concentration in the gas phase and it becomes in equilibrium with the oxygen surface concentration, C_s . Assuming constant oxygen flux through the SiAlON film, the oxygen concentration at the SiAlON / CrO_x interface, C_i , dictates the concentration gradient across the CrO_x layer. If one also assumes that the oxidation rate at the Cr / CrO_x interface is proportional to the concentration, C_o , one arrives at the expected expression for the time dependent evolution of the CrO_x thickness that is linear in short times and parabolic at longer times. Examples of the oxygen concentration gradients are shown in Figure 18 for a Si-Al-N rich and a Si-Al-O rich film. In the N-rich case, the oxygen diffusion rate through the SiAlON is much faster than the O-rich case, and hence the Cr would oxidize at a faster rate.

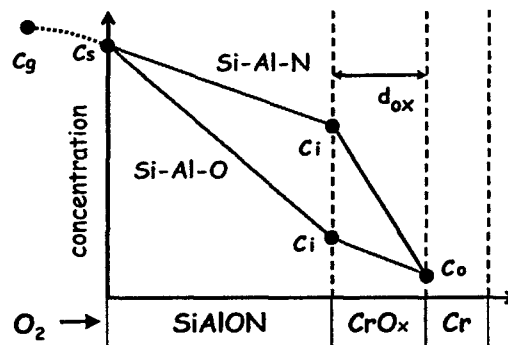
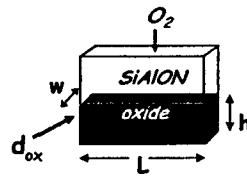


Figure 18 Model of the various oxygen concentrations that dictate the oxidation rate of a Cr sensor lying beneath a SiAlON film. The Cr oxidation from the underlying sapphire substrate is assumed to negligible.

Within a layer by layer oxide growth approximation, the CrO_x thickness will grow, thereby decreasing the thickness of the metallic Cr pattern. As shown in Figure 19, the conductance is inversely proportional to the resistance, and the conductance of the Cr sensor will decrease as the Cr thickness ($h - d_{ox}$) decreases. Following the Deal-Groves oxide theory,³⁴ the CrO_x thickness will follow parabolic rate behavior in the limit of long times, and will be proportional to

³⁴ B.E. Deal and A.S. Grove, J. Appl. Phys. 36 (1965) 3770

the square root of time. The parabolic oxidation rate constant, B , depends on the diffusion constant, D , the oxygen concentration at the interface, C_i , and the number density of oxygen atoms in the oxide, η_{ox} .



$$C(t) = \frac{\text{conductance}}{\text{resistance}} = \frac{1}{R(t)} = \frac{w(h - d_{ox})}{\rho L} \quad d_{ox} \sim \sqrt{Bt}$$

$$\text{parabolic oxidation rate constant} \quad B = \frac{2 D C_i}{\eta_{ox}}$$

Figure 19 The resistance change of the Cr sensor depends on the thickness of the metallic Cr layer, which decreases as a high resistance CrO_x layer forms via oxygen diffusion through the SiAlON film.

When the data in Figure 17b is plotted as conductance versus the square root of time (Figure 20), a linear region is found over about a 6 day time interval. According to the analysis in Figure 19, the linear relationship is

$$C(t) = \frac{wh}{\rho L} - \frac{w\sqrt{B}}{\rho L} \sqrt{t} \quad \text{or} \quad C = a - b\sqrt{t}$$

where a is the intercept and b is the slope. Applying this procedure to the data in Figure 17b results in a measurement of the parabolic rate constant $B = 4 \times 10^{-20} \text{ m}^2/\text{s}$ at 1000°C . This oxidation rate constant, which directly reflects the oxygen concentration arriving at the SiAlON / CrO_x interface (i.e. C_i) is extremely small (several orders of magnitude smaller than the rate of thermal oxidation of Si), which illustrates that rate limiting oxygen diffusion through the SiAlON film is extremely slow.

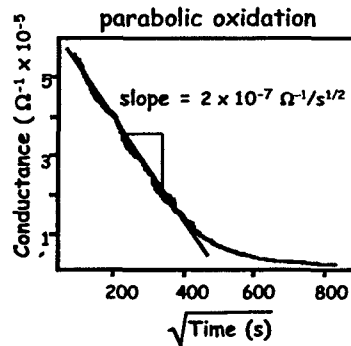


Figure 20 Analysis of sensor data in Fig. 17b in terms of conductance versus square root of time which yields a parabolic oxidation rate constant $B = 4 \times 10^{-20} \text{ m}^2/\text{s}$.

It is somewhat surprising that a simple diffusion model accurately fits the Cr sensor data, but the fact that parabolic behavior is observed for a time period of over six days gives credence to the hypothesis that the oxygen diffusion through the SiAlON is the rate limiting step. Analysis of the conductance changes of the Cr sensor at shorter times (< 10 hours) indicated that a simple linear or parabolic oxidation model was not appropriate. This result indicates that effects such as variable oxygen flux through the SiAlON, non layer-by-layer oxide growth, oxidation reactions at the Cr / sapphire interface, or other rate limiting steps may be important in the early stages.

The behavior of the Ni-Cr sensor (Fig. 17a) also does not follow the simple parabolic oxidation model. In the very early stages (< 1 hour), resistance changes related to the Curie transition in Ni-Cr³⁵ were observed, and the transitions in the resistance curves at later stages may be related to the preferential oxidation of Cr versus Ni in the sensor film. Further tests with different Ni-Cr compositions would be needed to study this aspect, but these experiments were not carried out in this work. Because of reliability issues with wire bonding, the contact resistance was also suspect. However, this was checked by using a Pt sensor pattern. Being inert to oxidation, the Pt sensor changed only from 75 Ω to 150 Ω during a four day annealing cycle at 1000°C, suggesting that contact resistance effects are negligible.

An experiment was conducted in which a 50 nm thick Al_2O_3 film was deposited on top of a β' SiAlON film to determine if an oxide cap would reduce or enhance the SiAlON oxidation rate. The results over a 20 day time period at 1000°C are shown in Figure 21. Both films exhibit parabolic oxidation kinetics during the first few days but the curves deviate at later times and also show some unexplained fluctuations. Despite the convoluted signatures in the sensor resistance, the results suggest that the Al_2O_3 cap accelerates the SiAlON oxidation process. This phenomenon may be explained if the oxygen concentration at the film surface (as shown by the model in Fig.18) is larger with the Al_2O_3 cap compared to the uncapped SiAlON film as a consequence of an oxygen adsorption barrier from the gas phase.

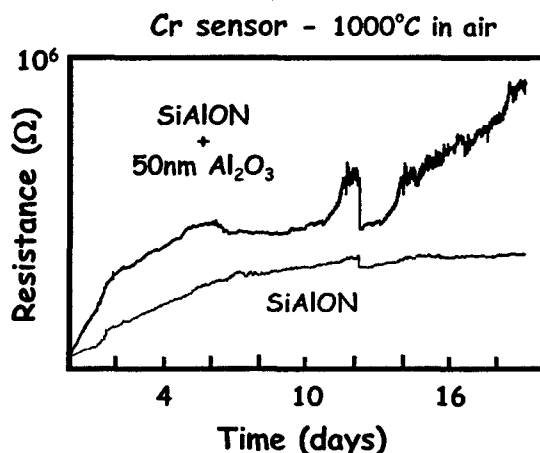


Figure 21 Comparison of Cr oxidation sensor response for a 1 μm thick β' SiAlON film with and without a 50 nm thick capping Al_2O_3 layer.

The previous result suggests that multilayer or gradient SiAlON film compositions may be an effective way to control the oxidation rate. However, these more complex experiments will require many more statistics with systematically varying parameters. The unreliable test platform and tedium of getting wire bonds that do not fail during testing precluded an exhaustive study in our work. As mentioned previously, a new microfabricated test platform based on a MEMS package that contains integral microheaters along with several temperature sensors and oxidation sensors would be one promising approach for the future.

³⁵ T.F. Smith, R.J. Tainsh, R.N. Shelton, W.E. Gardner, J. Phys. F: Met. Phys. 5 (1975) L96

5. Film Performance in Oxygen Plasma and Vacuum Annealing Environments

5.1 Interaction with ECR-Generated Oxygen Radicals

The SiAlON films were exposed to highly reactive oxygen radical species generated from an electron cyclotron resonance (ECR) oxygen plasma source. This treatment mimics the environment that SiAlON materials would be exposed to in the upper atmosphere in aerospace applications. The ECR source produces ~ 20 eV O^* radicals as well as O_2^+ ions at a pressure of 10^{-4} torr. XPS analysis was performed after ECR exposure to measure changes in surface stoichiometry. Figure 22 shows the surface oxidation of a β' SiAlON film at 50 and 1000°C after a one hour ECR exposure. The film becomes oxidized but at a much slower rate compared to annealing in atmospheric air. As a result of the ECR treatment, the N_{1s} XPS also exhibited a peak at 5 eV higher binding energy characteristic of local $N-O_3$ bonding (see Section 3.2).

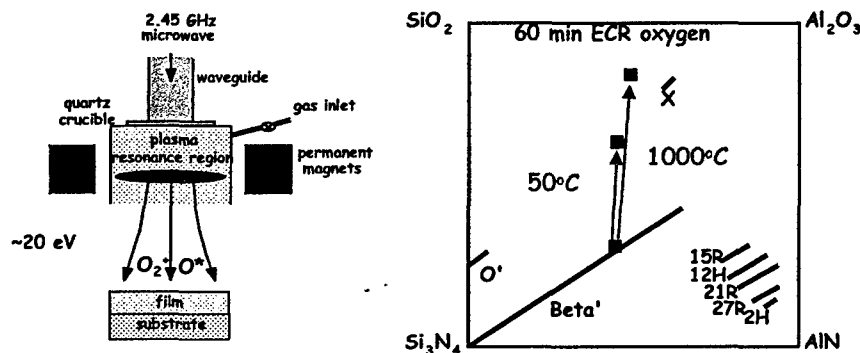


Figure 22 Low energy O^* and O_2^+ ions generated from an electron cyclotron resonance (ECR) plasma caused surface oxidation of the SiAlON films at room temperature.

5.2 Ultra-high Vacuum Annealing

SiAlON films were annealed up to 1000°C for several hours in vacuum environments ranging from 10^{-10} to 10^{-6} torr; at the higher pressures the main components were H_2O vapor and CO . Following annealing, XPS analysis indicated minimal changes in surface stoichiometry. This result is significant in that there is no segregation or loss of nitrogen at elevated temperatures. Reflection high energy electron diffraction (RHEED) and x-ray diffraction (XRD) indicated that the films remained amorphous for all annealing conditions.

6. Major Conclusions

SiAlON thin film structures deposited by RF magnetron co-sputtering of Al and Si targets in $Ar/O_2/N_2$ mixtures are promising smooth glassy coating materials for $>1000^\circ C$ aeronautic and aerospace applications. The SiAlON films remain amorphous in high temperature environments and exhibit excellent wear resistant behavior, particularly for nitrogen-rich compositions. However, the SiAlON films become oxidized during thermal treatments in oxygen environments. An *in situ* interfacial oxidation sensor embedded into the SiAlON coating demonstrated that the oxidation rate is relatively slow, and the material performance can be sustained for several weeks above 1000°C. Compositionally graded coatings may lead to improved oxidation resistance, but additional testing must be carried out to fully evaluate these materials and transition them into reliable service in Air Force systems. New initiatives to transition these SiAlON films into application environments are currently being pursued (see Section 7).

7. Technology Transfer to AFRL and Industry

- Nanomechanical properties of β' composition SiAlON films were characterized in January 2004 by Dr. Andrei Rar, Metals & Ceramics Division, Oak Ridge National Laboratory (Oak Ridge, TN). Nanoindenter measurements indicated that the film modulus for a 1.1 μm thick film was 272 GPa. Measurements on thinner films were also attempted but they were complicated by contributions from the sapphire substrate making the values difficult to interpret.
- The excellent wear resistance of our SiAlON films makes them potential passivation layers for sensor devices even at room temperature. In collaboration with BiODE Inc. (Westbrook, ME), we have deposited 200 nm thick SiAlON coatings onto prototype acoustic wave viscosity sensors being manufactured by BiODE and sold to industries to measure viscosity of inks and solders. The SiAlON film is being evaluated as a potential replacement for amorphous carbon passivation layers currently used at BiODE.
- The functionality of SiAlON coatings deposited onto carbon nozzles being used in thrusters is being explored in collaboration with Applied Thermal Sciences Inc. (Sanford, ME). Feasibility experiments are underway to simply evaluate the degradation of SiAlON coatings after extreme thermal treatments using the gas injection nozzles.
- Initiated through our presentation at the 52nd AVS Symposium in Boston, we have begun collaboration with Dr. Nazlim Bagcivan, Head of the PVD Technology Group at RWTH Aachen University, Germany to measure thermal shock behavior of our SiAlON films. Five different compositions of 1 μm thick SiAlON films have been deposited onto polished disks of a Ni-based superalloy provided by the Aachen group. The lifetime of these coatings will soon be measured in Aachen to determine how thermal shock performance is correlated to SiAlON composition, and to compare the SiAlON performance to other coatings developed in their laboratory. A visit to their lab in Aachen, Germany, by R.J. Lad is anticipated in July 2006 following his attendance at the 11th International Chemical Sensors Meeting in Brescia, Italy.
- A collaboration has recently been established with Dr. Andrey Voevodin from the Materials and Manufacturing Directorate at the Air Force Research Laboratory to evaluate the wear behavior of our SiAlON coatings using the high temperature pin-on-disk apparatus at AFRL. 1 μm thick SiAlON films on sapphire substrates have been prepared and they await measurement by Dr. Voevodin's group. Also, several discussions have been carried out to determine if the embedded interfacial oxidation sensor developed in this grant or related sensors of this type could be utilized for *in situ* measurements of tribological coating degradation during service.
- A new project at UMaine has been funded by the Air Force Research Laboratory, Materials and Manufacturing Directorate (AFRL/MLLP) to develop "Microwave Acoustic Sensors for Condition Based Maintenance in Harsh Environments". (PIs: Mauricio Pereira da Cunha and R.J. Lad) A visit to AFRL in January 2006 has resulted in several new collaborations and extensions of the SiAlON research. The immediate focus of the new project is to demonstrate the performance of a high temperature (1000°C) sensor based on langasite (LGS) piezoelectric crystals. Future directions involve the need to passivate the LGS sensor surface and SiAlON coatings are being considered for this purpose. Discussions on this topic are continuing with Mr. Craig Neslen and Dr. Joseph van Nostrand at AFRL/MLLP.

8. Research Publications and Presentations

Publications

"Synthesis and Characterization of SiAlON Thin Film Coatings," J.I. Krassikoff, G.P. Bernhardt, M. Call, T.A. Dunn, D.D. More, R.J. Lad, Society of Vacuum Coaters Tech. Proceedings 46, 627 (2003)

"SiAlON Thin Films for High Temperature Applications," J.I. Krassikoff, M.S. Thesis, University of Maine (2006)

"Chemical Bonding Effects in SiAlON Thin Films," J.I. Krassikoff, S. Rivers, R.J. Lad, Thin Solid Films (submitted 2006)

"High Temperature Oxidation of SiAlON Thin Film Coatings Evaluated by an Embedded Oxidation Sensor," S. Rivers, G. Bernhardt, C.J. Bocchino, J.I. Krassikoff, R.J. Lad, Surface and Coatings Technology (submitted 2006)

Presentations

"Multifunctional Silicon Aluminum Oxynitride (SiAlON) Thin Film Coatings for High Temperature Applications," 27th Annual Cocoa Beach Conference on Advanced Ceramics & Composites, Cocoa Beach, FL, Jan. 31, 2003 (talk by R.J. Lad)

"Synthesis and Characterization of SiAlON Thin Film Coatings," 46th Annual Technical Conference of the Society of Vacuum Coaters, San Francisco, CA, May 5, 2003 (poster by J.I. Krassikoff).

"Synthesis and High Temperature Performance of SiAlON Thin Film Coatings," AVS 50th International Symposium, Baltimore, MD, Nov. 3, 2003 (talk by R.J. Lad)

"Oxidation and Wear Behavior of Nanostructured SiAlON Thin Film Coatings," 29th International Conference on Advanced Ceramics & Composites, Cocoa Beach, FL, January 26, 2005 (talk by R.J. Lad)

"Multifunctional Silicon Aluminum Oxynitride (SiAlON) Ceramic Coatings for High Temperature Applications," AFOSR Ceramics Program Review, Wintergreen, VA, August 16, 2004 (talk by R.J. Lad)

"Defect Characterization of Ceramic Thin Films Using Surface Analysis Techniques," Army Workshop on Advanced Active Thin Film Materials for Next Generation of Meso-Micro Scale Army Applications, May 10, 2005, Destin, FL (talk by D.J. Frankel)

"Synthesis and Characterization of Multifunctional SiAlON Thin Films," Workshop on Multifunctional Material Stoichiometry, Jackson Hole, WY, July 18, 2005 (talk by R.J. Lad)

"Multifunctional SiAlON Ceramic Coatings for High Temperature Applications," AVS 52nd International Symposium, Boston, MA, October 30, 2005 (talk by R.J. Lad)

"Sensor Technology for High Temperature Applications," Wright-Patterson Air Force Research Laboratory, Dayton, OH, January 11, 2006 (talk by R.J. Lad and M. P. da Cunha)

"Protective SiAlON Coating with Embedded High Temperature Corrosion Sensor," 11th International Meeting on Chemical Sensors, Brescia, Italy, July 16-19, 2006 (submitted)

9. Personnel Involved in the Project

Faculty:

- Robert J. Lad (PI and Professor of Physics) - project director
- Steven Rivers - Visiting Professor of Physics (on sabbatical from Rhode Island College)

Research Staff:

- George Bernhardt (Research Scientist) - film synthesis and characterization
- Michael Call (Research Technician) - photolithography, film synthesis

Graduate Students:

- John Krassikoff (M.S. degree in Physics) - film synthesis and characterization

Undergraduate Students:

- Daesha More (undergraduate Physics major) -- Auger electron spectroscopy / depth profiling
- Tyler Dunn (undergraduate Physics major) -- atomic force microscopy, pin-on-disk testing
- Darren Southworth (undergraduate Physics major) -- multilayer film deposition