JOURNAL OF MATERIALS SCIENCE 27 (1992) 5504–5508

Oxidation characteristics of artificially layered Fe/Al and Fe/Mg thin films

S. VEENA KUMARI, V. K. VAIDYAN
Department of Physics, University of Kerala, Trivandrum 695 581, India
K. G. SATHYANARAYANA
Regional Research Laboratory CSIR, Trivandrum 695 019, India

Investigations were carried out on the oxidation characteristics of artificially layered Fe/Al and Fe/Mg thin films using X-ray diffraction and Raman spectroscopy at 303, 473, 673 and 773 K in the laboratory atmosphere. X-ray diffractograms and Raman spectra reveal diffusion phenomena occurring in Fe/Al thin films. Individual oxides and a spinel-phase $MgFe_2O_4$, were the oxidation products in Fe/Mg multilayers while intermetallics were found to be present in the Fe/Al system at 773 K, in addition to $FeAl_2O_4$.

1. Introduction

Recently, there has been a great interest in artificially layered materials which do not exist in nature. Multilayers of metallic films are commonly used to establish electrical contacts to silicon wafers. Artificially layered structures have unique structural [1], magnetic [2] and electronic [3] properties with a wide range of applications. Remarkable features of multilayered thin films are the atomistic, electronic structure of interfaces and the two-dimensional behaviour in electrical, magnetic, superconducting and mechanical properties [4, 5]. When the layer thickness approaches the nanometre range, interfacial atomic interaction becomes significant and is of interest in magnetic materials [6]. The decay, the phase transition from amorphous to crystalline, depends strongly on annealing conditions and the crystallographic structure of the film. For example, the layered structure of Co/Mo films remained intact after annealing to 700 K [7]. The order of deposition is also an important factor, and it has been found to influence the microstructure and diffusional properties of thin-film couples [8]. A quantitative theoretical investigation carried out by Hsu [9] on layered structures indicates the growth of the oxide layer to be cation-diffusion controlled. An excellent phenomenological analysis has been presented by Ge Wang *et al.* [10] on the growth of multilayered structures.

The present study investigated the oxidation characteristics of artificially layered Fe/Al and Fe/Mg thin films. Iron, aluminium and magnesium are very good systems in which to study physical mechanisms, and systems of mutually soluble Fe/Al and insoluble Fe/Mg surfaces were investigated using X-ray diffraction and Raman spectroscopy.

2. Experimental procedure

Artificially layered thin films of Fe/Al and Fe/Mg were prepared on glass substrates by successive thermal evaporation under a vacuum of about 10^{-5} torr from independent sources. Two sets of samples were prepared in each pair. In one set, iron was deposited first and then aluminium so that the aluminium was the top layer (Fe/Al). The total number of bilayers was adjusted to obtain a total thickness of about 50 nm. In the other set, the sequence of deposition was reversed, the top layer being iron (Al/Fe). The same procedure was used for preparing Fe/Mg and Mg/Fe layers. These samples were oxidized in the laboratory atmosphere at 303, 473, 673 and 773 K for 2 h. X-ray lattice parameter measurements were made with a Philips PW 1710 diffractometer using CoK_α radiation in the range 2θ from 20°–60°. Raman spectra of these samples were recorded using SPEX Ramlog 1401 with a laser power of 50 mW.

3. Results and discussion

3.1. X-ray diffraction analysis

The properties of multilayer film depends on the structure and properties of components, mutual solubility and the possible formation of intermetallic compounds between the components. The deposition of an overlayer on the material modifies the surface of the underlayer and consequently changes the properties of the film. The X-ray diffraction (XRD) patterns of Fe/Al and Al/Fe films at 303, 473, 673 and 773 K are given in Fig. 1 and Table I, respectively. The data values are compared with the ASTM card file and the previous work [11].

The general feature observed in Fe/Al and Al/Fe samples is the gradual intensity decrease for the diffraction peaks corresponding to $2\theta \approx 52.6°$ and 45°, which were identified as α-Fe and Al_2O_3. The decrease in intensity after annealing is clearly an indication of structural relaxation and interdiffusion phenomena occurring in both the samples. Belser [12] showed the

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TABLE I X-ray diffraction data and identification of oxides of Al/Fe and Fe/Al artificially layered films at different temperatures

Temperature (K)	Al/Fe		Fe/Al	
	Lattice spacing (nm)	Identification	Lattice spacing (nm)	Identification
303	0.187	α-Fe_2O_3	0.186	α-Fe_2O_3
	0.189	α-Fe_2O_3	0.189	α-Fe_2O_3
	0.202	α-Fe	0.202	α-Fe
	0.235	Al_2O_3	0.233	Al_2O_3
473	0.210	α-Fe	0.202	α-Fe
			0.217	Fe_3O_4
	0.238	Al_2O_3	0.233	Al_2O_3
673	0.203	α-Fe	0.202	α-Fe
	0.234	Al_2O_3	0.234	Al_2O_3
	0.253	Fe_2O_3	0.252	Fe_2O_3
	0.296	$FeAl_2O_4$	0.296	$FeAl_2O_4$
773	0.203	α-Fe	0.185	Al_3Fe
	0.210	AlFe	0.202	α-Fe
	0.221	Al_3Fe	0.234	Al_2O_3
	0.234	Al_2O_3	0.252	Fe_2O_3
	0.253	Fe_2O_3	0.313	$FeAl_2O_4$
	0.274	Fe_3Al	0.389	Al_3Fe
	0.297	$FeAl_2O_4$	0.416	Al_3Fe

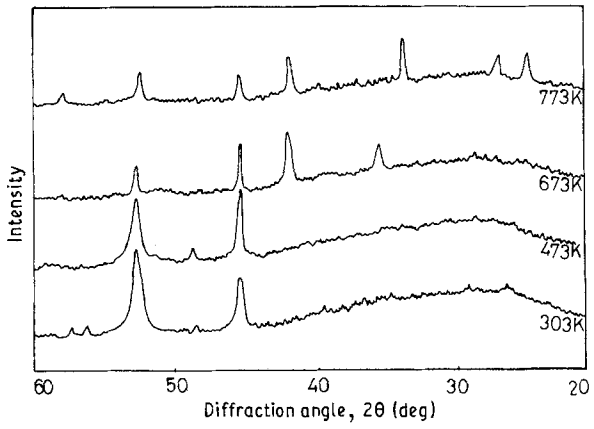

Figure 1 CoK_α XRD of oxidized Fe/Al thin films at 303, 473, 673 and 773 K.

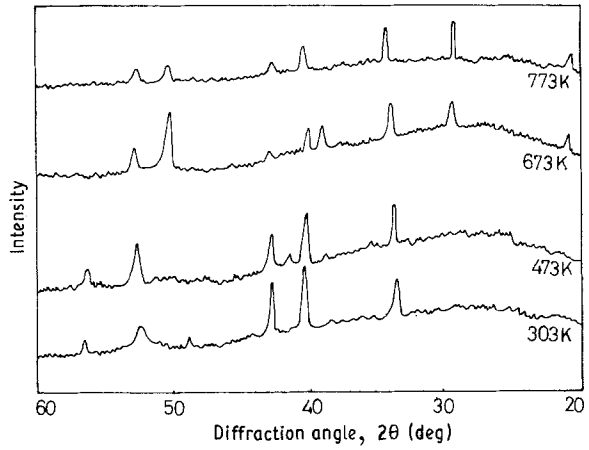

Figure 2 XRD scan of oxidized Fe/Mg thin films at 303, 473, 673 and 773 K.

presence of an oxide at the interface for aluminium-based couples. For Al/Fe, the major diffraction peaks are for α-Fe_2O_3 and Al_2O_3. Additional peaks are observed at 773 K, which are attributed to intermetallics Al_3Fe, Fe_3Al, AlFe and a spinel phase $FeAl_2O_4$. For Fe/Al at low temperatures, the presence of Fe_3O_4 is also detected. Al_3Fe peaks are observed for both Fe/Al and Al/Fe but Fe_3Al was detected for Al/Fe. Because the interfacial layer at boundaries plays an important role in determining the kind of compound formed, a change in layer sequence can alter the products formed. Iron oxidation involves outward diffusion of iron ions and the inward diffusion of oxygen ions. Oxide growth mechanisms allow for both anion and cation movements [13]. The oxidation occurring on Al/Fe and Fe/Al causes continued diffusion during annealing and creates chemical potential sinks. In the case of Fe/Al layered films, several processes can occur during air annealing: (i) interdiffusion of iron and aluminium, (ii) diffusion of oxygen through iron and aluminium, (iii) oxidation near the interface. At low temperatures (< 473 K) Al_2O_3 may act as a diffusion barrier. At higher temperatures this barrier is overcome by diffusion of iron and oxygen ions which leads to the formation of $FeAl_2O_4$. The discrepancy observed in the number of diffraction lines in Fe/Al and Al/Fe is attributed to the slight difference in thickness of the multilayering.

Table II gives the *d*-spacings and identification of oxides present in Fe/Mg and Mg/Fe thin film samples. The CoK_α diffraction scan of Fe/Mg films oxidized at 303, 473, 673 and 773 K for 2 h in the laboratory atmosphere is shown in Fig. 2. The available literature on Fe/Mg systems shows no intermetallic formation and no mutual solubility [14]. The air annealing of Fe/Mg and Mg/Fe films exhibited α-Fe, MgO, Fe_2O_3, Fe_3O_4 and $MgFe_2O_4$. An increase in diffraction intensity is observed for Mg/Fe and Fe/Mg corresponding to $2\theta \approx 52.4°$ up to 473 K. The intensity increase is appreciable compared with that between 673 and

TABLE II X-ray diffraction data and identification of oxides of Mg/Fe and Fe/Mg artificially layered films at different temperatures

Temperature (K)	Mg/Fe		Fe/Mg	
	Lattice spacing (nm)	Identification	Lattice spacing (nm)	Identification
303	0.191	Mg	0.190	Mg
	0.203	α-Fe	0.201	α-Fe
	0.246	MgO	0.216	?
	0.262	α-Fe_2O_3	0.245	MgO
	0.268	α-Fe_2O_3	0.260	α-Fe_2O_3
	0.279	MgO	0.268	α-Fe_2O_3
			0.310	Fe_3O_4
473	0.191	Mg	0.190	Mg
	0.203	α-Fe	0.202	α-Fe
	0.246	MgO	0.245	MgO
	0.262	α-Fe_2O_3	0.260	α-Fe_2O_3
	0.268	α-Fe_2O_3	0.269	α-Fe_2O_3
	0.279	MgO	0.301	Fe_3O_4
673	0.191	Mg	0.202	α-Fe
	0.203	α-Fe	0.210	?
	0.212	MgO	0.245	MgO
	0.246	MgO	0.262	Fe_2O_3
	0.253	$MgFe_2O_4$	0.268	Fe_2O_3
	0.263	Fe_2O_3	0.301	Fe_3O_4
	0.269	Fe_2O_3	0.355	MgO
	0.370	MgO	0.477	$MgFe_2O_4$
	0.482	$MgFe_2O_4$		
773	0.207	α-Fe	0.202	α-Fe
	0.212	MgO	0.210	?
	0.251	$MgFe_2O_4$	0.245	MgO
	0.272	Fe_2O_3	0.262	Fe_2O_3
	0.296	Fe_3O_4	0.301	Fe_3O_4
	0.323	Fe_2O_3	0.355	MgO
	0.368	MgO	0.477	$MgFe_2O_4$
	0.482	$MgFe_2O_4$		

TABLE III Raman frequencies of Al/Fe and Fe/Al artificially layered thin films at various temperatures

Raman frequencies of Al/Fe (cm^{-1})					Raman frequencies of Fe/Al (cm^{-1})				
303	473	673	773 K	Identification	303	473	673	773 K	Identification
221	–	–	–	α-Fe_2O_3	221	–	–	–	α-Fe_2O_3
					250	248	–	–	α-Fe_2O_3
284	284	280	280	$FeAl_2O_4$	282	283	284	284	$FeAl_2O_4$
–	–	370	370	Al_2O_3	320	320	320	–	α-Fe
					370	370	370	–	Al_2O_3
					385	–	–	–	Al_2O_3
					415	415	415	–	$FeAl_2O_4$
441	441	440	440	$FeAl_2O_4$	440	440	440	440	$FeAl_2O_4$
449	449	448	448	$FeAl_2O_4$	461	462	460	460	$FeAl_2O_4$
501	498	497	497	α-Fe_2O_3	500	500	500	500	α-Fe_2O_3
542	–	–	–	Fe_3O_4	553	–	–	–	Al_2O_3
610	610	607	607	Al_2O_3	607	610	586	586	Al_2O_3
–	–	–	624	$FeAl_2O_4$					
–	–	–	670	Fe_3O_4	676	676	674	674	Fe_3O_4
775	775	773	771	?	771	771	773	770	?
					789	790	790	790	?

773 K. A decrease in intensity is observed for MgO and Fe_2O_3 up to 473 K for Mg/Fe, and above 673 K, an increase in intensity is seen for $MgFe_2O_4$ and α-Fe_2O_3. Even though the coexistence of magnesium with iron oxide is unlikely, the presence of magnesium in the film cannot be ruled out from the X-ray diffraction data. Above 473 K the presence of MgO is detected. The diffusion of iron ions into MgO is strongly concentration dependent and chemical diffusivities and diffusional activation energy increase with increasing iron concentration. Electron paramagnetic and optical absorption measurements carried out by

Diggle and Vijh [15] suggests a change in activation energy with increasing iron content in the FeO/MgO system resulting from the existence of Fe^{3+} on tetrahedral sites, which leads to the formation of $MgFe_2O_4$ precipitates and hence increasing energy for the motion of magnesium ions. Mixing of iron and magnesium ions in the lattice occurs due to annealing, as indicated by the decreasing intensity for $2\theta \approx 52°$. Because FeO is stable only above 843 K, the presence of FeO is discarded. The phases identified include MgO, Fe_2O_3, Fe_3O_4 and a spinel compound $MgFe_2O_4$.

3.2. Raman spectroscopy

Single and multilayer coatings exhibit optical properties controlled by chemical bonding and inherent microstructure results from particular deposition techniques. The application of Raman spectroscopy to characterize such materials is attractive [16–18]. Fig. 3 and Table III show the Raman spectra of artificially layered Fe/Al and Raman frequencies of Fe/Al and Al/Fe with possible assignments. Raman features are similar to that observed in X-ray diffraction. Interdiffusion occurring between iron and aluminium layers has caused the intensity decrease for Raman lines at 771, 500, 440, 282 cm^{-1} and for the broad band at 676 cm^{-1} for Fe/Al and 775, 500, 441 and 284 cm^{-1} for Al/Fe. A frequency shift of about 10 cm^{-1} to a lower wave number is observed for 600 cm^{-1}. This is attributed to the intrinsic stress developed or due to the difference in thermal expansivity of the film and the substrate. The decrease in the number of Raman lines due to annealing indicates the ordering of the phases formed in Fe/Al, while an increase in the number of Raman lines in Al/Fe is attributed to the enhanced oxidation of iron. The oxidation products are α-Fe, Fe_2O_3, Al_2O_3, Fe_3O_4 and $FeAl_2O_4$. The unidentified lines in Table III are assigned to the intermetallics.

The Raman frequencies for Fe/Mg and Mg/Fe oxidized at 303, 473, 673 and 773 K are summarized in Table IV. There is no difference observed in the two spectra. Frequency shifts of 10 cm^{-1} are observed for 440, 590, 695 and 795 cm^{-1} and are attributed to the oxidation products MgO, $MgFe_2O_4$ and α-Fe_2O_3. Fe_3O_4 could not be detected in Fe/Mg and Mg/Fe samples using Raman spectroscopy.

TABLE IV Raman frequencies of Fe/Mg and Mg/Fe artificially layered thin films at various temperatures

Raman frequencies (cm^{-1})				Identification
303 K	473 K	673 K	773 K	
221	221	221	221	
248	–	–	–	α-Fe_2O_3
265	–	–	–	
270	–	–	–	α-Fe
290	–	–	–	
–	–	281	281	$MgFe_2O_4$
308	308	308	308	MgO
358	–	–	–	
–	–	385	385	$MgFe_2O_4$
–	392	–	–	α-Fe_2O_3
420	417	–	–	
–	–	440	450	MgO
482	504	500	500	α-Fe_2O_3
–	555	556	556	MgO
590	590	607	607	$MgFe_2O_4$
640	648	–	–	α-Fe
695	690	675	675	?
722	732	732	735	?
775	779	776	–	α-Fe_2O_3

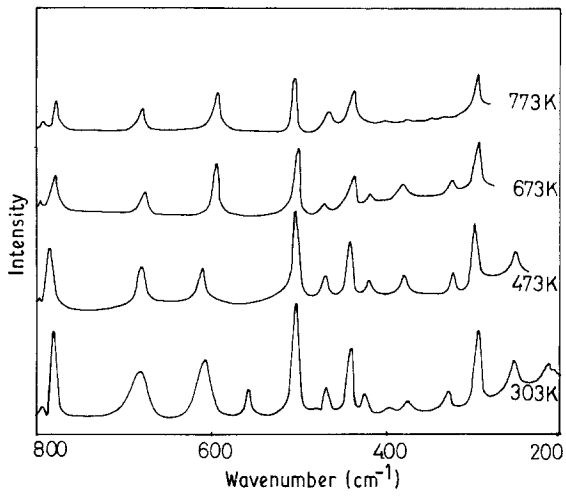

Figure 3 Raman spectra of Fe/Al thin films oxidized at 303, 473, 673 and 773 K.

4. Conclusions

Oxidation studies carried out on artificially layered Fe/Al and Fe/Mg thin films by X-ray diffraction and Raman spectroscopy exhibited diffusion phenomena. Individual oxides and spinel-phase $MgFe_2O_4$ are the oxidation products in Fe/Mg while intermetallics are present in Fe/Al.

Acknowledgement

One of the authors (SVK) thanks the Council of Scientific and Industiral Research for the award of a Senior Research Fellowship.

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Received 20 June 1991
and accepted 7 February 1992