Bull. Mater. Sci., Vol. 24, No. 6, December 2001, pp. 583–586. © Indian Academy of Sciences.

# Preparation of Sm–Ru bimetallic alloy films on Ru(0001) surface by vapour-deposition and annealing

**G RANGA RAO* and H NOZOYE†**

Department of Chemistry, Indian Institute of Technology, Chennai 600 036, India
†National Institute of Materials and Chemical Research, 1-1 Higashi, Tsukuba, Ibaraki 305, Japan

MS received 16 January 2001

**Abstract. Sm–Ru intermetallic surface alloy films were prepared by vacuum deposition and annealing of rare earth Sm on single crystal Ru(0001) surface. The Ru 3*d* and Sm 3*d* core level spectra clearly show the formation of surface alloy layers. XPS measurements on surface alloy film revealed an induced peak in the Ru 3*d* region at lower binding energy by 1 eV compared to the bulk Ru (elemental) suggesting an electronic effect of alloying and Sm–Ru bond formation. The Sm $3d_{5/2}$ photoemission peak of Sm film consists of strong features characteristic of Sm(II) with electron configuration $4f^6$ $(5d\ 6s)^2$ and Sm(III) with electron configuration $4f^5$ $(5d\ 6s)^3$. It is observed that the Sm(II) feature decreases in intensity upon alloy formation with surface Ru atoms. Oxidation of these films with carbon monoxide indicates alloy breakdown due to the oxidation of Sm atoms selectively. Alloy oxidation also shows a clear shift of Sm $3d_{5/2}$ feature.**

**Keywords. Surface film; XPS; rare earth; bimetallic alloy; ruthenium.**

## 1. Introduction

The growth and surface chemistry of thin alloy films is a subject of great interest from the point of view of their basic scientific understanding and applications in areas such as adsorption and catalysis, hydrogen storage and surface magnetism (Netzer and Bertel 1982; Ranga Rao 1998; Ramstad *et al* 1999). Intermetallic films involving rare earth (RE) and transition metals (TM), in particular, have been investigated to elucidate the physical and chemical properties such as surface structure and alloying, valence changes, microfaceting, formation of hydride phases, exotic surface magnetic layers and reactivity (Gasgnier 1995; Ranga Rao *et al* 1995; Sato *et al* 2000). Rare earth epitaxial films are utilized as precursors to prepare good quality rare earth oxide films for surface studies of model catalysts on well-defined metal substrates. Such novel approaches of surface modelling have been reported for oxide films such as $Al_2O_3$, $TiO_2$, ZnO, MgO and $CeO_2$ (Campbell 1997; Gunter *et al* 1997; Persaud and Madey 1997; Henry 1998). Like transition metal oxide overlayers, ordered rare earth oxide layers may be synthesized selectively by the oxidation of RE/TM alloy films, leaving the transition metal in its metallic state. This procedure has been adopted in preparing ordered ultra-thin $La_2O_3$-like film on Cu(111) (Asha and Nix 1995), $CeO_2$ on Pt(111) (Schierbaum 1998) and $Ce_2O_3$-like oxide on W(110) (Vescovo and Carbone 1996). The intermetallic alloys of $Pt_3Ce_7$ were also used as precursors to design highly dispersed and active $Pt/CeO_2$ catalysts (Hardacre *et al* 1996).

Sm/Ru(0001) intermetallic system has been of recent interest in this area of research (Ranga Rao *et al* 1995; Kuriyama *et al* 1997). Sm exhibits mixed valence (number of electrons in the *ds* valence band) which are sensitive to chemical environment. It is trivalent ($4f^5[ds]^3$ configuration) in the bulk and divalent ($4f^6[ds]^2$ configuration) on the surface (Wertheim and Crecelius 1978). In the atomic state Sm is divalent but due to the gain in cohesive energy, it is trivalent in the bulk of metallic Sm. It usually forms surface overlayers on several metals such as Al, Cr, Cu, Mo, Nb, Ni, Pd, Pt, Ta and W (Ranga Rao *et al* 1995; Strisland *et al* 1998). However, on some of these metal surfaces (e.g. Cu, Ni, Pt, Al and Ru), Sm forms alloys under favourable conditions. The technique often employed in characterizing rare earth surface alloy films is photoelectron spectroscopy. Other spectroscopic methods like low energy ion scattering (LEIS), scanning tunneling microscopy (STM) and Auger electron spectroscopy (AES) have also been extensively used. X-ray photoelectron spectroscopy (XPS) is suitable to study the core level shifts, while UPS is mainly employed to investigate valence levels of metal overlayers as function of coverage, *q*. Photoelectron spectroscopy provides direct evidence on electronic perturbations involved in the chemical bond formation and charge transfer effects in the surface overlayers (Santra and Rao 1995) and bimetallic films (Ranga Rao 1998).

*Author for correspondence

In this paper, we report on the preparation of good quality Sm/Ru bimetallic films starting from Sm vapour deposit at 120 K under UHV conditions. The chemical interaction between Sm and Ru atoms has been studied by XPS. We illustrate that careful annealing of the deposit may produce surface intermetallic phases. These phases are found to be very sensitive to CO exposures and may be used to produce thin model $Sm_2O_3$ films on Ru substrate.

## 2. Experimental

The vapour deposition and surface analysis of Sm layers on Ru(0001) crystal were carried out in the preparation and analysis chambers of VG ESCALAB Mark II electron spectrometer. The Ru crystal was mounted on liquid nitrogen cooled manipulator using tantalum wires. The temperature can be varied between 95 K and 1500 K and was measured by a thermocouple spot welded to the crystal. Pure and collimated Sm vapour was generated by heating pure Sm resistively inside the preparation chamber at a base pressure of $1 \times 10^{-10}$ mbar. The contamination due to hydrogen and oxygen has been avoided carefully by outgassing both Ru crystal as well as the Sm source at elevated temperatures in UHV for many hours. To clean the surface, Ru crystal was first annealed and then flashed to ~ 1500 K. Ru 3*d*, O1*s* and Sm 3*d* XPS regions were monitored using Al $K_a$ radiation at an analyser pass energy, 20 eV. No detectable contamination of surfaces occurred during the experiments. Annealing of Sm/Ru interface was carried out at desired temperature under UHV conditions.

## 3. Results and discussion

The general method of preparing RM/TM surface alloy films is the deposition of the vapour obtained by evaporation of pure rare earth samples in ultrahigh vacuum. It is, however, difficult to prepare clean rare earth-based alloy films because of high reactivity of rare earth metals towards oxygen and other gases. We have used resistive heating of clean Sm metal piece for contamination free deposition and ensured that the pressure during the evaporation never exceeded ~ $7 \times 10^{-10}$ mbar. By this method, a thin layer of Sm was deposited on the Ru surface at 120 K for about 25 min. The amount of Sm deposit is estimated to be ~ 3 monolayers based on Sm/Ru 3*d* ratio and TPD calibration curve reported earlier (Ranga Rao *et al* 1995). The corresponding Sm-covered Ru surface was annealed carefully at various temperatures. Annealing of the Sm-covered Ru produces interesting results which are summarized in figure 1. The plots represent the integrated Sm 3*d* and Ru 3*d* XPS intensities at a fixed emission angle as function of annealing temperature. The interface annealing was carried out for about five min at each data point and was cooled to ~ 300 K before recording XPS spectra. Shirley background subtraction was used for calculating the 3*d* intensities. It is interesting to see that the Sm 3*d* vs temperature curve shows a step-wise fall of Sm 3*d* intensity while the Ru 3*d* vs temperature curve exhibits a step-wise raise of Ru 3*d* intensity with temperature. This indicates systematic changes both in Sm and Ru atomic concentrations in the top layers of the Ru surface due to interdiffusion. Several TM/TM and RM/TM metal systems have been reported to show the tendency to form surface alloys by interdiffusion and faceting (Bardi 1994; Guan *et al* 1995; Ranga Rao *et al* 1995; Ranga Rao 1998). However, in the case of Sm on Ru, the step-wise diffusion process, as seen in figure 1, is pointing towards the formation of intermetallic compounds of certain fixed compositions. Similar observations have been reported on Al/Ru(0001) and Sm/Cu(111) systems (Wu *et al* 1995). The decrease and increase in intensities respectively of Sm 3*d* and Ru 3*d* are not linear or continuous but occur in step-wise manner around 120–450 K, 450–650 K and 650–850 K (see figure 1). The low temperature plateau is essentially due to elemental Sm deposit that does not diffuse into Ru subsurface in this temperature range. The interdiffusion is setting in above 450 K and the second

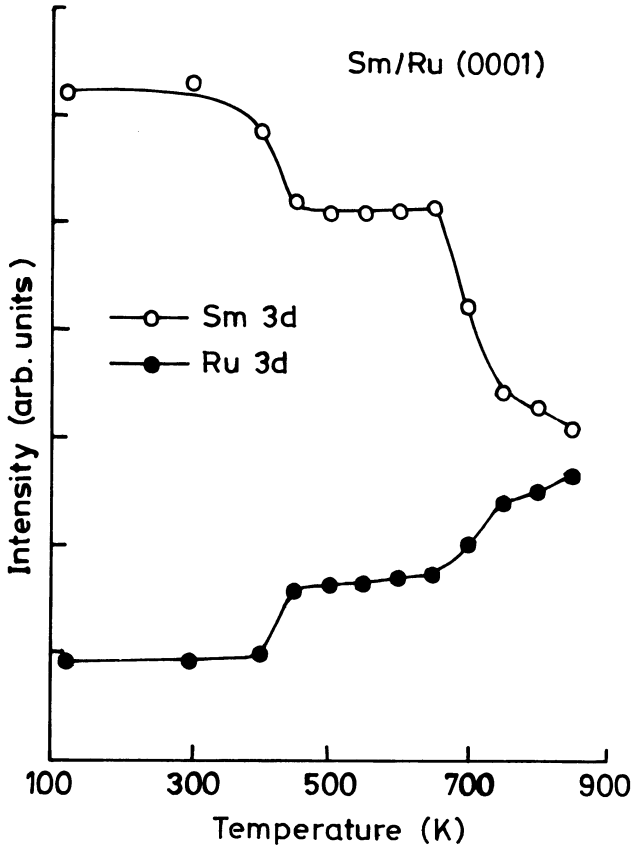


**Figure 1.** Sm 3*d* and Ru 3*d* intensity variations as function of annealing temperature of Sm deposit on Ru(0001).

and third steps can be attributed to the formation of intermetallic alloys of particular compositions. Above 850 K, the alloy phases decompose leading to Sm desorption.

In order to check the elemental character of Sm and alloy formation upon annealing, Ru 3*d* XPS region was monitored. Figure 2 shows the Ru 3*d* spectra from Ru surface after Sm deposition at 120 K, annealing at 500 K and then CO exposure at 105 K. The Ru 3*d* spectrum (figure 2a) at 120 K shows only the elemental Ru signal at 280 eV and there is no spectral evidence of alloying between Sm and Ru atoms at this temperature. Alloying of Ru with other metals (e.g. Al and Sm) usually gives a Ru 3*d* peak at ~ 279 eV and it is also seen clearly in the Ru 3*d* doublet (figure 2b) at 500 K. The induced intense peak at 279 eV occurs above 450 K indicating the growth of an alloy phase due to diffusion at elevated temperatures. Such a process is schematically shown in figure 3.

Alloy formation can also be confirmed from the detailed XPS scan of Sm $3d_{5/2}$ region shown in figure 4. The Sm $3d_{5/2}$ spectrum of Sm deposit at 120 K (figure 4a) shows characteristic divalent ($4f^6$) component between 1070 and 1080 eV and trivalent ($4f^5$) component between 1080 and 1090 eV. When the surface is annealed at 500 K, the intensity of the divalent component is reduced considerably indicating that there is a cohesive bond between surface Sm and Ru atoms. This observation therefore confirms the surface diffusion and bonding between Sm and Ru atoms at elevated temperatures.

The reactivity of the Sm–Ru surface alloy film is checked by exposing it to one Langmuir (1 L) CO gas at $10^{-8}$ torr and 105 K. The corresponding Ru 3*d* and Sm $3d_{5/2}$ spectra are presented in figures 2c and 4c, respectively. The Ru 3*d* spectrum after CO exposure shows the reversal of peak intensities of elemental Ru and alloyed Ru. This is due to the fact that the Sm–Ru alloy decomposes in the presence of CO and forms surface Sm–oxide/carbide. The oxidation of Sm component is also seen clearly in the Sm $3d_{5/2}$ spectra in figure 4. The full width at half maximum (FWHM) increases from spectrum 4*a* to spectrum 4*c* ($3{\cdot}6 \rightarrow 3{\cdot}8 \rightarrow 4{\cdot}4$ eV). In addition, there is a $4f^5$ peak shift to higher binding energy by about 1 eV. These changes in the Sm $3d_{5/2}$ spectral characteristics strongly suggest the Sm oxidation upon CO exposure. It is, therefore, possible that Sm–Ru alloy films

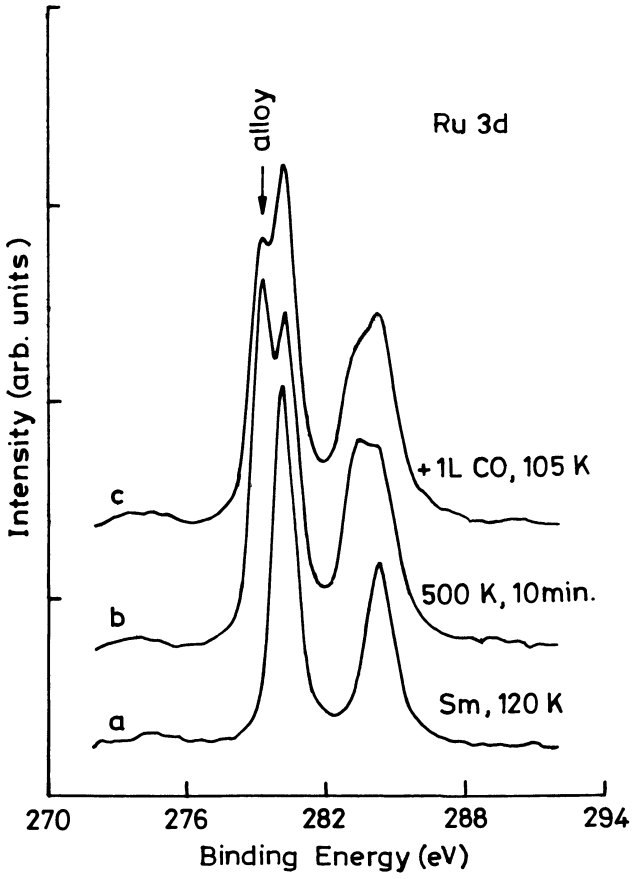


**Figure 2.** Ru 3*d* region monitored from Ru surface: a. Sm deposit at 120 K, b. annealed at 500 K and c. exposed to CO at 105 K.

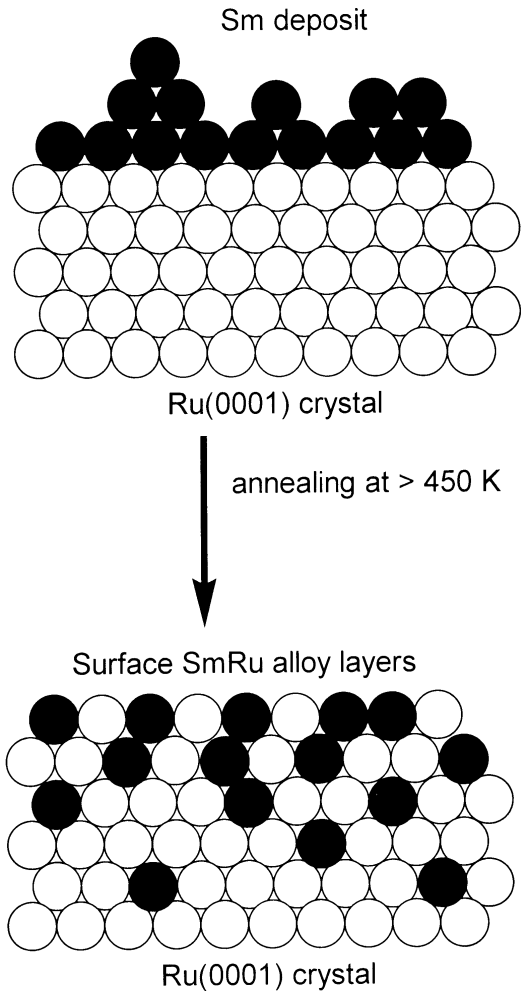


**Figure 3.** Diffusion process leading to surface alloy formation on Ru(0001) surface at elevated temperatures.

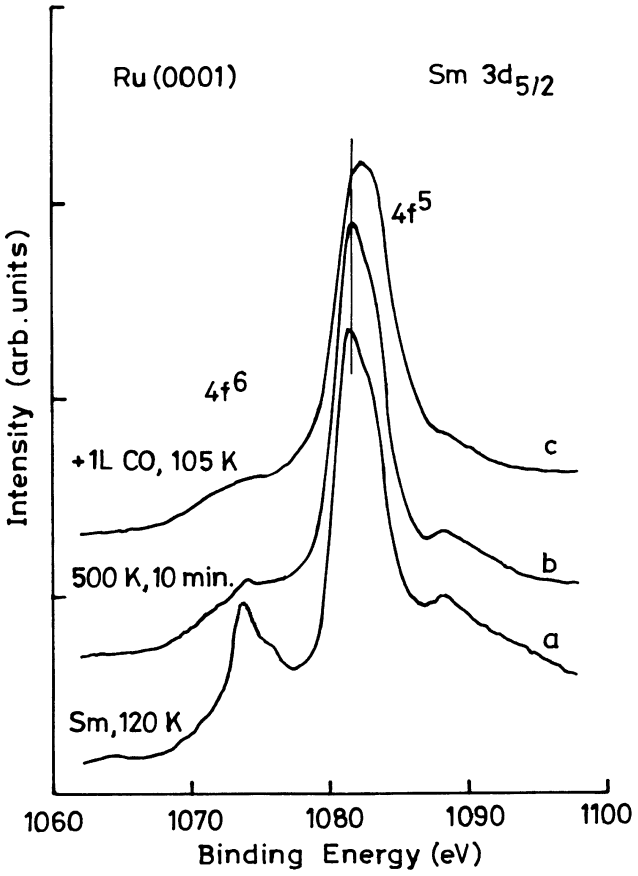


**Figure 4.** Sm $3d_{5/2}$ monitored from Ru surface under the same conditions as in figure 2.

can be oxidized fully to produce clean stoichiometric $Sm_2O_3$ films on Ru(0001). This method was employed for the synthesis of stoichiometric $Al_2O_3$ films on Ru(0001) surface as well (Wu *et al* 1995).

## 4. Conclusions

Sm deposition on Ru(0001) surface at 120 K and annealing at elevated temperatures (> 450 K) results in the formation of ultra-thin Sm–Ru bimetallic alloy films. This is confirmed by the induced Ru 3*d* feature at lower binding energy (– 1·0 eV) and the near disappearance of $4f^6$ configuration of Sm atoms. Thermal annealing at various temperatures indicates the formation of binary intermetallic phases in the range 450–850 K. Alloy films are found to be reactive and can be decomposed to prepare $Sm_2O_3$ films covering Ru substrate for surface studies.

## Acknowledgements

One of the authors (GRR) would like to thank the Japan Industrial Technology Association for research invitation and Dr T Tamaki for permission to access the experimental facilities in the Department of Molecular Engineering at NIMC.

## References

Asha A M D and Nix R M 1995 *Surf. Sci.* **322** 41
Bardi U 1994 *Rep. Prog. Phys.* 939
Campbell C T 1997 *Surf. Sci. Repts* **27** 1
Gasgnier M 1995 *Handbook on the physics and chemistry of rare earths* (eds) K A Gschneidner Jr. and L Eyring (Amsterdam: Elsevier Science) **20** pp 105–206
Guan J, Campbell R A and Madey T E 1995 *Surf. Sci.* **341** 311
Gunter P L J, Niemantsverdriet J W H, Ribeiro F H and Somorjai G A 1997 *Catal. Rev. Sci. Eng.* **39** 77
Hardacre C, Rayment T and Lambert R M 1996 *J. Catal.* **158** 102
Henry C R 1998 *Surf. Sci. Repts* **31** 231
Kuriyama T, Kunimori K and Nozoye H 1997 *J. Phys. Chem.* **101** 11172
Netzer F P and Bertel 1982 *Handbook on the physics and chemistry of rare earths* (eds) K A Gschneidner Jr. and L Eyring (Amsterdam: North Holland) **5** pp 217–319
Persaud R and Madey T E 1997 *Growth and properties of ultrathin epitaxial layers* (eds) D A King and D P Woodruff (Amsterdam: Elsevier Science) pp 407–447
Ramstad A, Strisland F, Raaen S, Worren T, Borg A and Berg C 1999 *Surf. Sci.* **425** 57
Ranga Rao G 1998 *Curr. Sci.* **75** 901 and references therein
Ranga Rao G, Kadowaki Y, Kondoh H and Nozoye H 1995 *Surf. Sci.* **327** 293
Santra A K and Rao C N R 1995 *Appl. Surf. Sci.* **84** 347
Sato N, Takayama M, Yoshimoto N and Yoshizawa M 2000 *Physica* **B281 & 282** 707
Schierbaum K D 1998 *Surf. Sci.* **399** 29
Strisland F, Ramstad A, Berg C and Raaen S 1998 *Surf. Sci.* **410** 344
Vescovo E and Carbone C 1996 *Phys. Rev.* **B53** 4142
Wertheim G K and Crecelius G 1978 *Phys. Rev. Letts* **40** 813
Wu Y, Tao H, Garfunkel, Madey T E and Shinn N D 1995 *Surf. Sci.* **336** 123