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Use of metastable, dissociated and charged gas species in synthesis: a low pressure analogue of the high pressure technique

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Oxidation of silver using microwave-induced oxygen plasma and oxygen-ozone gas mixture was studied as a function of temperature and partial pressure. The oxide Ag_2O was formed at temperatures well above its normal decomposition temperature in oxygen plasma at a pressure of 5 Pa. The higher oxide AgO_{1-x} was formed in $O_2 + O_3$ gas mixtures at lower temperatures. The oxygen chemical potentials for the oxidation of Ag to Ag_2O, Ag_2O to AgO_{1-x} and AgO to Ag_2O_3 were evaluated from thermodynamic data and compared with the experimental results to obtain information on the chemical potential of oxygen in microwave plasma and gases containing ozone. The oxygen potential of the gas phase in microwave plasma operating at a pressure of 5 Pa was found to be in excess of 36 kJ/mol at 750 K. This is equivalent to a pressure of diatomic oxygen gas greater than 3×10^7 Pa. In the $O_2 + O_3$ mixture at ambient pressure containing 5 mole percent O_3, the oxygen potential is $\sim$112 kJ/mol at 465 K. The equivalent pressure of diatomic oxygen is $\sim 4 \times 10^{17}$ Pa. Thus, metastable species such as O_3 or charged species such as O^- present in plasma can be used as a powerful reagent for the syntheses of metastable oxides. Similar techniques can be used for other metastable inorganic solids such as nitrides for functional applications. © *2000 Kluwer Academic Publishers*

1. Introduction

Several technologically important oxides and nitrides with unique functional properties are unstable at ambient pressure of oxygen or nitrogen at elevated temperatures. They are often synthesized in oxygen or nitrogen gas at high pressures. For device applications, thin films of these materials are needed, often in multi-layer assemblies. While the classical high pressure synthetic technique is suitable for preparation of relatively large quantities of polycrystalline material, it is not compatible with current technologies employed in the fabrication of electronic devices. It is therefore useful to develop alternate low pressure routes for the syntheses of metastable oxides and nitrides at moderately elevated temperatures.

Diatomic oxygen and nitrogen gas can be dissociated by a variety of methods to monatomic or ionized species. These species exist at energies considerably higher than that of the diatomic species. They can be continuously generated by coupling to an external energy source. A steady state concentration of these unstable species can be obtained in the gas phase, when the rate of production and rate of recombination are judiciously balanced. Plasmas containing charged species can be readily generated by arc discharge, by inductive coupling to a radio frequency generator (RF), or by microwave discharge. The high energy species present in the plasma are generally more reactive. The thermodynamic driving force for reactions involving dissociated or ionized oxygen species is far greater than that for the reactions involving stable diatomic species. From this point of view, these metastable species at low pressures are analogous to high pressure diatomic oxygen or nitrogen.

Examined in this article is the use of oxygen plasma at reduced pressure and metastable ozone gas at ambient pressure for the syntheses of oxides, which are unstable at ambient pressure of diatomic oxygen at the reaction temperature. It is shown that oxygen plasma and ozone at moderate temperatures (350 to 750 K) provide the same thermodynamic driving force for synthesis of oxides as diatomic oxygen at pressures upto 10^{10} MPa.

2. Gibbs energies of dissociated, ionized and metastable forms of oxygen

Standard Gibbs energies of formation of O, O^+, O^-, O_2^+, O_2^- and O_3 are displayed in Fig. 1 as a function of temperature. Thermodynamic data for all the

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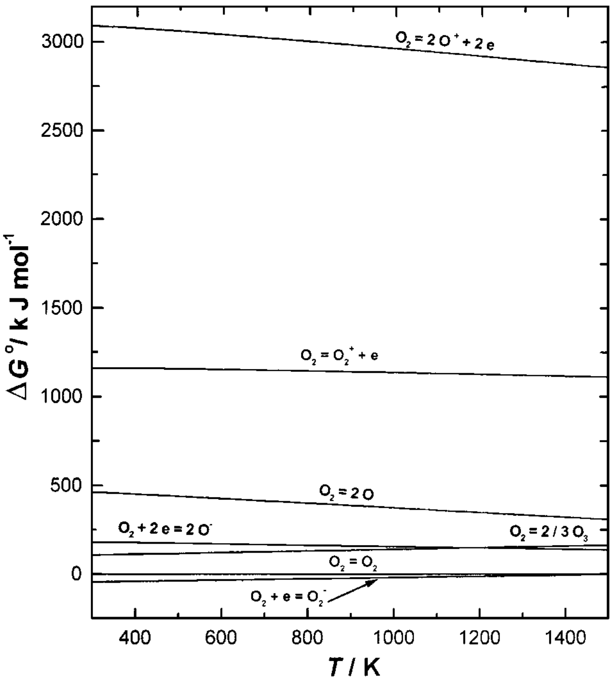

Figure 1 Temperature dependence of standard Gibbs energies of formation of dissociated and ionized oxygen species from one mole of diatomic oxygen gas.

species are taken from JANAF tables [1]. All the reactions involve one mole of diatomic oxygen, so that standard Gibbs energy change, $\Delta G^\circ = \Delta\mu_{O_2} = RT \ln P_{O_2}$, when the metastable species are in their standard states. Thus, positive Gibbs energy changes are associated with high pressure diatomic oxygen, when the other species involved in the reactions are at standard pressure ($P^\circ = 0.1$ MPa). Standard Gibbs energies of formation of O^- and O_3 from one mole of diatomic oxygen are of comparable magnitude. Production of neutral monatomic species requires higher energy. Reactions for generating positively charged species are highly endothermic. In Fig. 1, data for only singly charged species are shown. Production of doubly charged positive ions require energies outside the range of Fig. 1. From energetic considerations, most predominant positive ion in the plasma is expected to be $O_2{}^+$. The predominant negative species in the oxygen plasma is probably $O_2{}^-$.

In oxygen plasma, the partial pressures of the dissociated and charged species are expected to be substantially below unity. The chemical potentials of oxygen ($\Delta\mu_{O_2} = RT \ln P_{O_2}$) corresponding to the unstable species at different partial pressures ($P/P^\circ = 1$, 10^{-1} and 10^{-2}) are shown in Fig. 2 as a function of temperature. The equilibrium chemical potential of diatomic oxygen decreases with decrease in partial pressures of the metastable species. Although unstable species do not physically generate diatomic oxygen molecules at high pressure, they maintain an equivalent oxygen potential in the gas phase which is available for oxidation.

3. Experimental aspects

Experiments were designed to test the oxidizing potential of oxygen-microwave plasma and ozone. Silver foils were exposed to the oxidizing gas at selected temperatures and the reaction products were identified using X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). Silver is known to form several oxides, Ag_2O, AgO_{1-x}, Ag_3O_4 and Ag_2O_3 as the pressure of the diatomic oxygen is increased above atmospheric at moderately high temperatures.

3.1. Experiments in microwave plasma

Experiments were carried out in a single mode waveguide attached to a microwave generator operating at 2.45 GHz frequency. Schematic diagram of the experimental setup is given in Fig. 3. A piece of pure silver foil of dimensions 5 × 5 × 0.01 mm was mounted on the quartz sample holder and placed in the microwave cavity. The chamber was evacuated to a pressure of ~2 Pa. Microwave power was slowly increased till pink coloured stable plasma was obtained. The microwave power level was 155 W ($V = 155$ V, $I = 1$ A). The foil was exposed to pink plasma for about two minutes at a pressure of 2 Pa. Then oxygen leak rate was increased until pressure increased to ~5 Pa. The colour of the plasma changed from pink to green in presence of oxygen. The plasma was extinguished at higher pressures. In presence of microwaves, alumina-sheathed thermocouple gave unstable temperature readings. The temperature measured immediately after switching off the plasma was ~750 K. The silver foil recovered after the experiment was found to have a black coating on the surface exposed to the plasma. XRD analysis of the coating revealed the presence of Ag_2O with a small amount of silver as shown in Fig. 4. There were no peaks corresponding to AgO in the XRD pattern. An XPS investigation of the oxide-coated surface was carried out using ESCALAB V spectrometer. The sample preparation chamber was at a base pressure of 2.7×10^{-8} Pa. Al K_α (1486.6 eV) radiation was employed for XPS and AUGER measurements. The spectra were recorded with pass energies of 50 eV. The binding energies (BE) were referred to Ag ($3d_{5/2}$) of pure silver (368.2 eV). Shown in Figs 5 to 7 are Ag(3d), O (1s) and Ag (MNN) spectra. For the Ag (3d) spectrum, the observed binding energy for Ag ($3d_{5/2}$) was 367.4 eV. Full width at half maximum (FWHM) for this peak was ~2 eV. BE value of 373.3 eV was observed for the Ag($3d_{3/2}$) energy level, which appeared as another well-defined peak with a FWHM of ~3 eV. The O (1s) spectrum recorded for the oxide-coated silver foil showed the characteristic intense peak of Ag_2O. There was no C (1s) peak in the spectrum. This confirmed the absence of carbonates in the sample. BE was 530.2 eV with FWHM equal to 3.5 eV. The characteristic satellite peaks associated with Ag ($3d_{5/2}$) and Ag ($3d_{3/2}$) as well as the O (1s) peak in the spectra for the AgO [2] were not observed in the present study. The nature of the Ag ($3d_{5/2}$), Ag ($3d_{3/2}$) and O (1s) spectra were very similar to that reported by Tjeng *et al.* [3] for Ag_2O. The BE values obtained in this study and those reported by Tjeng *et al.* [3] are compared in Table I.

Auger analysis of the oxide coated silver foil showed an intense doublet with an energy separation of 5.6 eV.

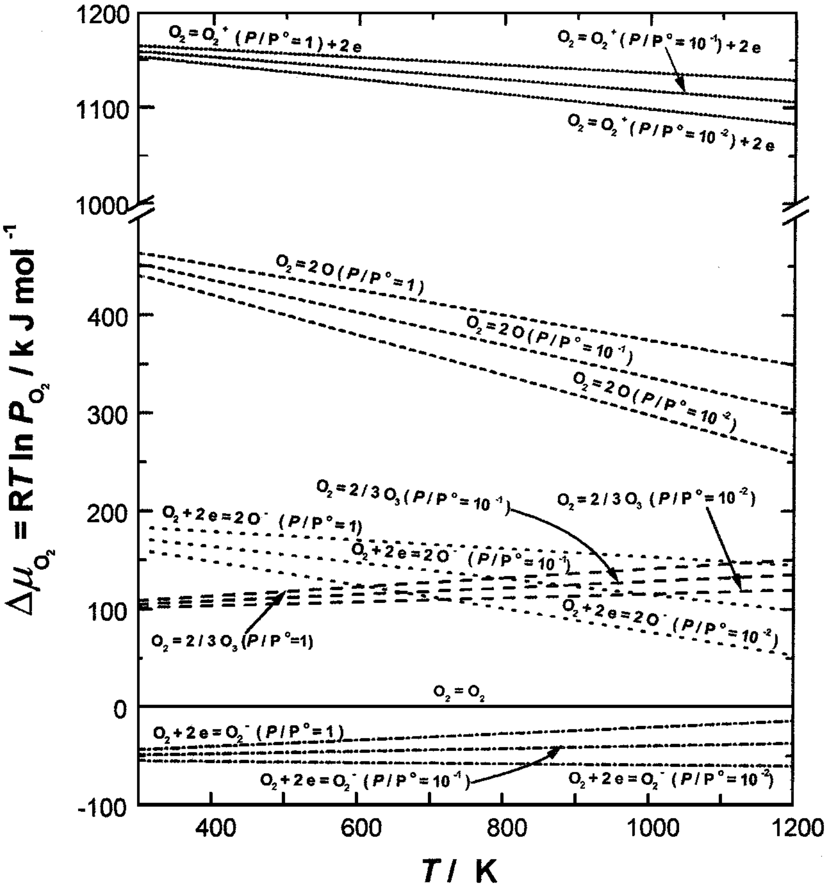

Figure 2 Oxygen potential associated with dissociated and ionic species at different partial pressures as a function of temperature.

TABLE I Comparison of the binding energy values of Ag (3d) and O (1s) spectra recorded for the oxide coated silver foil and Ag_2O

Electron energy level	This study	Tjeng *et al.* [3]
Ag ($3d_{5/2}$) (BE, eV)	367.4 (±0.2)	367.6 (±0.2)
Ag ($3d_{3/2}$) (BE, eV)	373.3 (±0.2)	373.6 (±0.2)
O (1s) (BE, eV)	530.2 (±0.2)	528.9 (±0.2)

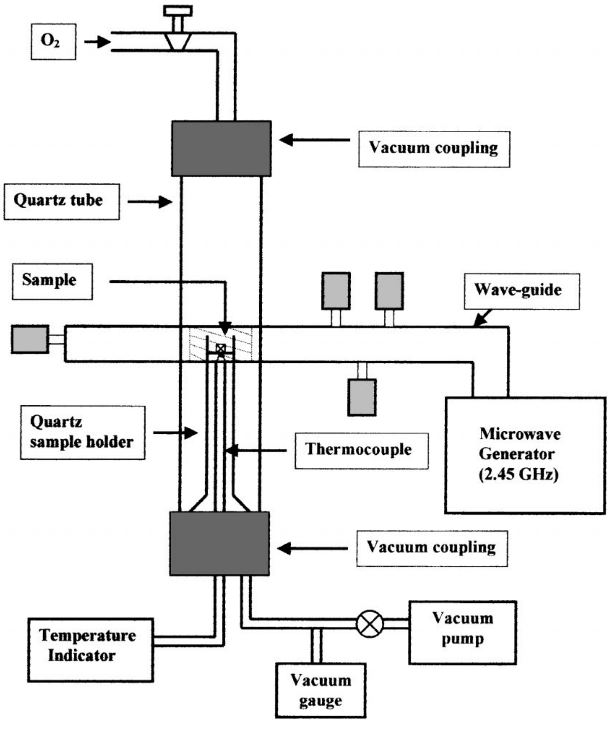

Figure 3 Schematic diagram of the experimental setup for studying oxidation of silver using microwave plasma.

The Auger electron energies obtained in this study for the oxide-coated silver foil were 349.7 (±0.2) eV ($M_5N_{45}N_{45}$) and 355.3 (±0.2) eV ($M_4N_{45}N_{45}$). The corresponding values reported by Tjeng *et al.* [3] for Ag_2O were 351.9 (±0.2) eV ($M_5N_{45}N_{45}$) and 357.3 (±0.2) eV ($M_4N_{45}N_{45}$), with a characteristic energy difference of 5.4 eV. The two peaks in the Auger spectrum observed in this study correspond to kinetic energies (KE) less than those reported by Tjeng *et al.* [3]. But the difference in energy between the doublet is comparable with that reported by Tjeng *et al.* [3] for the compound Ag_2O. Thus, both XRD and XPS studies on oxide-coated silver foil indicate that the oxide phase is Ag_2O.

A few oxidation studies of Ag in microwave plasma were conducted at a power level of 350 W. A small silver pellet of 5 mm diameter and 3 mm thickness was placed in a quartz cup and exposed to microwave plasma using the same experimental setup as shown in Fig. 3. At the higher power level the metal was found to melt. After switching off the power, Ag melt was found adherent to the quartz tube. The XRD pattern of the sample scratched out from the crucible showed peaks corresponding to Ag_2O, Ag and traces of Ag_2CO_3. Since Ag_2O was present mainly at the melt/crucible

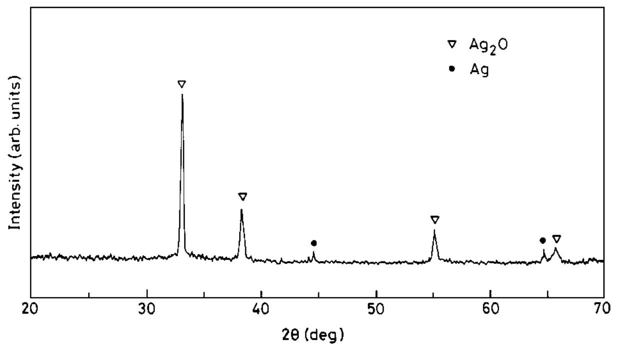

Figure 4 XRD pattern silver foil oxidized in microwave plasma at 750 K.

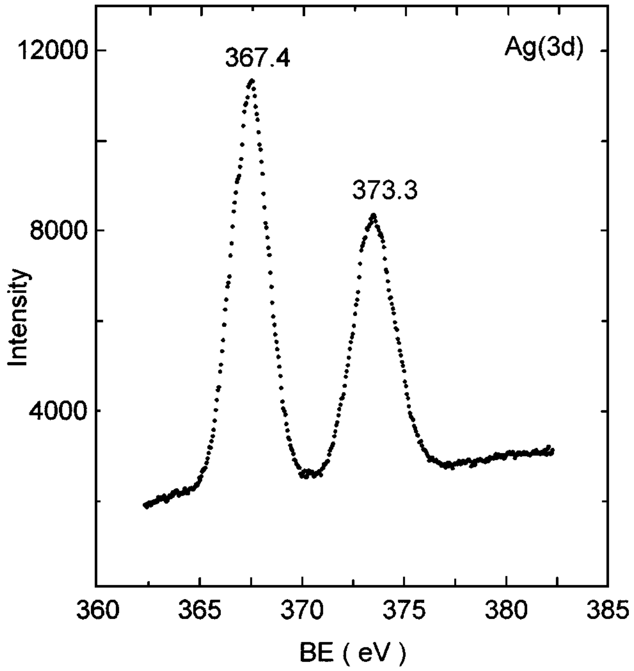

Figure 5 Ag (3d) X-ray photoelectron spectrum (XPS) of the oxide coated silver foil obtained from microwave experiment at 750 K.

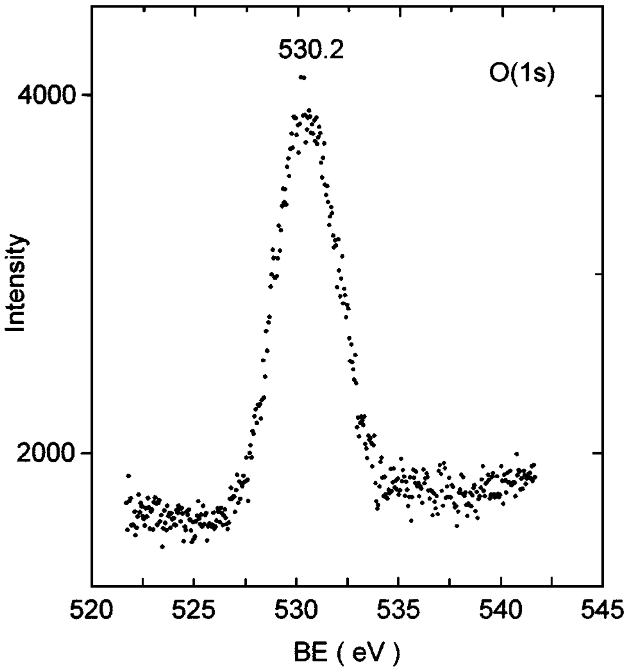

Figure 6 O (1s) XPS of oxide coated silver foil.

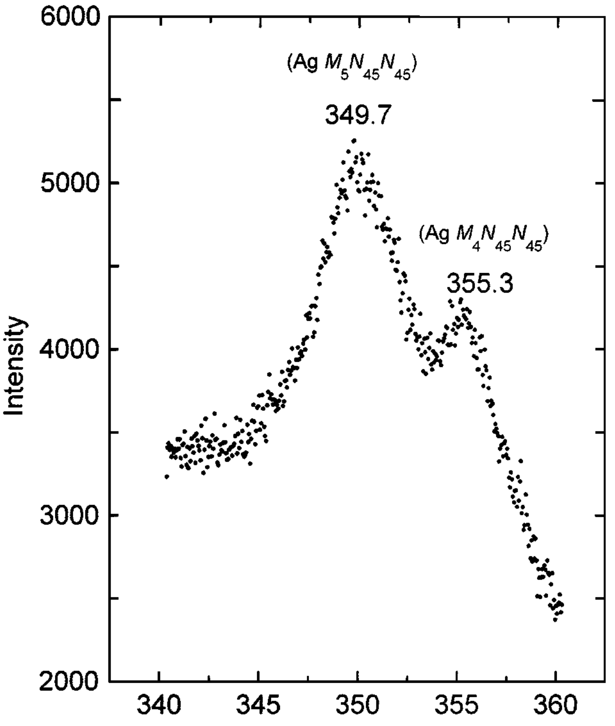

Figure 7 Result of the Auger analysis of the oxide coated silver foil, Ag (MNN).

interface, it probably formed during the solidification of liquid Ag-O solution. According to the phase diagram for the Ag-O system, the eutectic temperature is 803 (±5) K. At this temperature, solid Ag coexists with liquid Ag-O solution containing 0.25 mole fraction of O and solid Ag_2O at an oxygen pressure of 5.3×10^7 Pa. Therefore, temperature of Ag metal at 350 W microwave power level must have been above 803 K.

3.2. Experiments in ozone

A commercial ozone generator was used to produce ozone in pure oxygen gas at ambient pressure. Ozone was produced by a discharge mechanism. Teflon or teflon-coated tubes and stopcocks were used to transport the gas containing ozone. Ozone was introduced into the reaction chamber through a water-cooled alumina tube. A copper coil, wound around the alumina tube, was used for water cooling. Cooling of the inlet gas was necessary to prevent decomposition of ozone before it is exposed to the charge in the crucible. Partial pressure (P/P^o) of ozone was varied from 0.01 to 0.05 by altering the applied current in the ozone generator at constant oxygen flow rate. The quartz reaction vessel was suspended in a Kanthal-wound resistance furnace as shown in Fig. 8. Fine powder (−300 mesh) of silver or Ag_2O contained in alumina crucible was placed at the bottom of the quartz container. A mixture of oxygen and ozone was introduced in close vicinity of the charge through the water-cooled alumina tube. The top end of the silica tube was closed with a gas-tight lid. The gas stream was sampled at the inlet and the outlet of the reaction chamber. About 10^{-5} m^3 of the gas mixture was extracted periodically for analysis of ozone by the wet chemical method. Ozone in the exit gas was completely decomposed by passing through a column

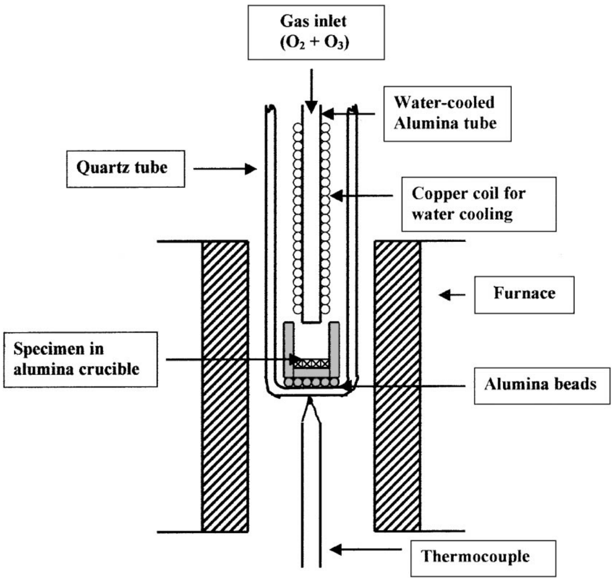

Figure 8 Schematic diagram of the apparatus used for oxidation studies of silver in gas mixtures containing ozone.

containing NaOH and Fe_2O_3 heated to ~500 K before release to the atmosphere. Experiments were conducted at gas flow rates varying from 5×10^{-6} to 10^{-5} m^3/s.

Experiments on the oxidation of Ag were conducted at 723 K for periods upto 7.2 ks in gas mixtures containing oxygen and ozone. The partial pressure of the ozone in the inlet gas was 0.03 and that in the exit gas was less than 2×10^{-4}. After exposure to ozone metallic silver became black. The XRD identified Ag_2O as a product of the reaction. The oxidation experiments were subsequently conducted as a function of temperature. Below 368 K, the oxidized sample contained a mixture of Ag_2O and AgO. At 368 K, the partial pressure of ozone in the exit gas was 0.021. AgO was also formed when a fine powder of Ag_2O was exposed to the gas containing 3 mole percent ozone. When the partial pressure of ozone in the inlet gas was increased to 0.05, AgO could be detected below 465 K.

4. Discussion

Thermodynamic properties of Ag_2O are reasonably well established at low temperatures. Gibbs energies of formation of Ag_2O upto 500 K are presented in the compilation of Pankratz [4]. In a recent review of thermodynamic properties of Ag-O system by Assal *et al.* [5, 6], data upto 773 K are presented based on high pressure studies on $Ag + Ag_2O$ equilibrium. The extrapolated data from the compilation of Pankratz at 800 K is in good agreement (±0.65 kJ/mol) with that recommended by Assal *et al.* [5, 6]. Ag_2O is stable in pure diatomic oxygen at standard pressure (P°) upto 470 K (±5) K.

Thermodynamic properties of AgO are relatively uncertain. Pankratz [4] has compiled data upto 500 K. For Ag_2O_3, thermodynamic data are available only at 298 K [7]. Using the data available in the literature,

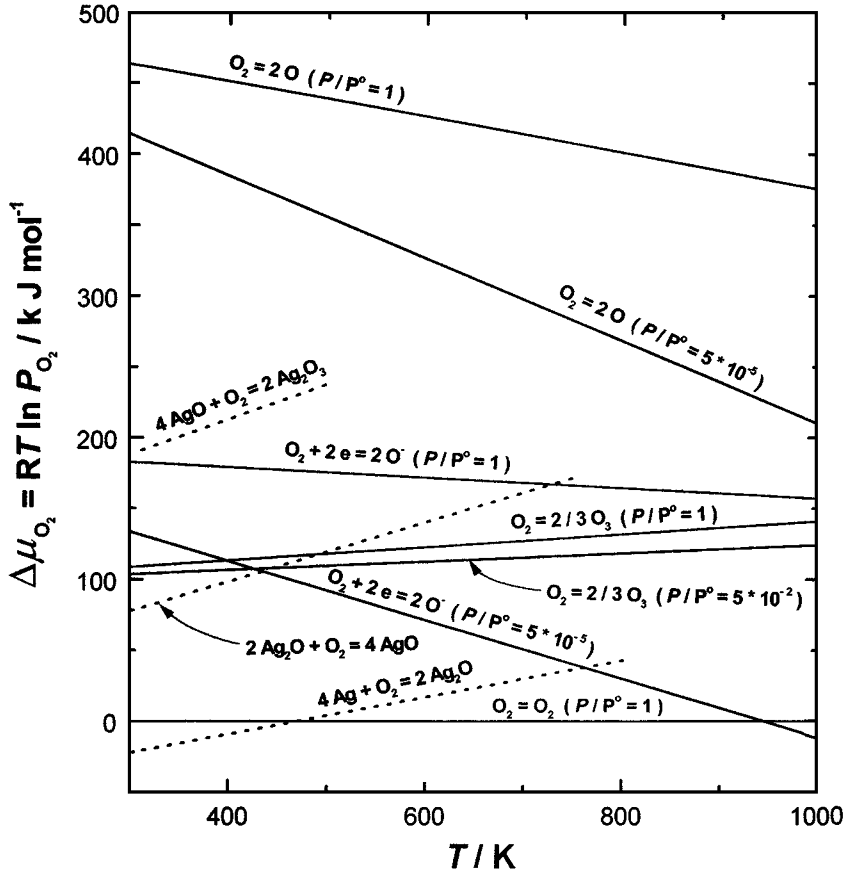

Figure 9 Temperature dependence of oxygen potential of oxidation of Ag to Ag_2O, Ag_2O to AgO and AgO to Ag_2O_3. Also shown in the diagram are the oxygen potentials associated with O and O^-at a partial pressure (P/P°) of 5×10^{-5} and ozone at a partial pressure (P/P°) of 5×10^{-2} corresponding to experimental conditions.

the oxygen potentials corresponding to $Ag + Ag_2O$, $Ag_2O + AgO$ and $AgO + Ag_2O_3$ are evaluated as a function of temperature (Fig. 9). Superimposed in this figure are the oxygen potentials defined by dissociated and charged species of oxygen at various partial pressures.

It is interesting to speculate which of the metastable ionized species in oxygen-microwave plasma is responsible for controlling the oxygen chemical potential. Since Ag_2O_3 was not formed in the microwave plasma at 750 K, inspection of the Fig. 9 suggests that neutral monatomic oxygen is unlikely to control the prevailing oxygen potential. The most likely species controlling the oxygen potential in the plasma is O^-, singly charged negative ion of monatomic oxygen. In Fig. 9, two lines corresponding to $O_2 + O^-$ equilibria are shown; one with O^- at atmospheric pressure and other with O^- at a partial pressure of 5×10^{-5} atm. The second probably resembles the conditions that prevailed during the microwave experiment.

Metallic silver was oxidized to Ag_2O in oxygen microwave plasma at 750 K. Therefore, the oxygen potential in plasma must be higher than that of $Ag + Ag_2O$ equilibrium. Thus oxygen microwave plasma at a total pressure of ~5 Pa generates an oxygen chemical potential in excess of ~36 kJ/mol or an equivalent pressure of diatomic oxygen greater than 3×10^7 Pa.

Experimental studies in $O_2 + O_3$ gas mixture containing 3 mole % O_3 at ambient pressure indicate that the oxygen potential in this gas is above that for $Ag + Ag_2O$ equilibrium at 723 K. The oxygen potential at 368 K was approximately the same as that for $Ag_2O + AgO$ equilibrium. Thus, the oxygen potential of the gas is ~92 kJ/mol and equivalent partial pressure of diatomic oxygen ~10^{18} Pa at 368 K.

At 5 mol % O_3 in O_2, AgO was formed at temperatures below 465 K. The corresponding oxygen potential is ~112 kJ/mol and equivalent pressure of diatomic oxygen 4×10^{17} Pa. This experimental finding is in good agreement with thermodynamic estimation shown in Fig. 9. The line for $O_2 + O_3$ equilibrium in the gas phase, with partial pressure of ozone equal to 0.05, intercepts the line for representing $Ag_2O + AgO$ equilibrium at $T = 450$ K. Thus gas mixtures containing small amounts of ozone can produce equivalent pressures of diatomic oxygen in excess of 10^{17} Pa or 10^{12} atm, well above what can be safely achieved in a high pressure reactor.

The principles outlined above can be adopted for the syntheses of nitrides. Ammonia gas, which is metastable at moderately high temperatures has been used for the nitrides. For example, Si_3N_4 films can be deposited from a gas mixture of silane and ammonia at reduced pressure using hot filament deposition reactor. Atomic (nascent) hydrogen produced by the dissociation of ammonia can reduce oxides that are invariably present on the surface of metals. Plasmas containing either nitrogen or nitrogen and hydrogen can be used for ion nitriding.

5. Conclusion

Oxidation of Ag to Ag_2O at 750 K in microwave plasma at a pressure of 5 Pa has been experimentally demonstrated. Similarly, oxidation of Ag to Ag_2O and AgO in ozone at a partial pressure of 0.05 at 465 K has been demonstrated. The chemical potentials of diatomic oxygen for $Ag + Ag_2O$, $Ag_2O + AgO$, $AgO + Ag_2O_3$ equilibria are compared with that in equilibrium with various metastable species O, O^- and O_3 under the experimental conditions. The comparison reveals that the most probable species in oxygen-microwave plasma is singly charged negative ions of monatomic oxygen, which generates an equivalent oxygen chemical potential of 36 kJ/mol or pressures equivalent to 3×10^7 Pa of diatomic oxygen at 750 K. Ozone at a partial pressure of 0.05 at 465 K has the oxidation potential equivalent to diatomic oxygen at pressure 4×10^{17} Pa. Thus, very high chemical potential of diatomic oxygen are generated in environment containing metastable species, facilitating syntheses of unstable oxides which can otherwise be produced only at extremely high pressures of diatomic oxygen gas. Similar methods can be used for the syntheses of nitrides using either ammonia or a nitrogen-plasma at moderately elevated temperatures.

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