

Plasma deposition and Auger studies of carbon impurities in zinc oxide

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A low pressure radio-frequency discharge in methane or a methane–oxygen mixture is used to deposit carbon species on the surface of compacted ZnO powder at 400° C. The carbon composition of the treated samples is examined in a separate Auger spectrometer system as the samples are heated in vacuum to 400° C, exposed at 400° C to oxygen, reannealed at the same temperature and subjected to argon ion bombardment. Evidence is presented that in the case of ZnO treated in methane–oxygen discharges, volume incorporation of carbon occurs and that this carbon moves to the surface of the sample in the course of subsequent vacuum heat treatment.

1. Introduction

There have been numerous references in the literature to the occurrence of carbon on vacuum heated surfaces of solid materials, for example, on the initially clean surfaces of semiconductors examined in ultra-high vacuum [1, 2]. A recent work describes a selective build-up of carbon impurity on ZnO surfaces during X-ray photoelectric analysis [3]. In this and in the earlier cases mentioned vacuum system contamination was given as the cause of the impurity build-up. Elsewhere, carbon levels in ZnO have been reported to be decreased by illumination of the oxide with radiation of energy equal to the ZnO band gap (365 nm) [4, 5]. In this result the photo-desorption of carbon dioxide was observed.

It would seem desirable that methods for controllably introducing carbon impurity be investigated. Electrical discharges in gaseous hydrocarbons have been studied extensively with regard to the formation of carbonaceous material (see e.g. the review [6]). Although there is little direct information on the nature of the excited species in these discharges a combination of the radicals CH, CH₂, and CH₃ is believed to be involved in the film deposition [7]. In the present work on ZnO a low pressure glow discharge in methane was used to deposit carbonaceous impurity on powder samples. The effects on the carbon content of the treated material of thermal

cycling, gas exposure and argon ion bombardment were studied by Auger spectroscopy combined with mass spectrometry.

2. Experimental details

An inductively coupled radio-frequency glow discharge in methane (flow rate $\sim 5 \text{ cm}^3 \text{ min}^{-1}$) at reduced pressure (~ 0.5 torr) was used to treat the ZnO powder samples. The latter were placed in proximity to the induction coil within the extended discharge region. The radio-frequency source used was a modified induction heating unit producing a maximum power output of 1 kW. Usually the ZnO powder (AR grade ex B.D.H., England) was compacted dry before treatment to form tablets of about 6 mm diameter by 1 mm thick, but in some cases the powder was dispersed in the silica sample boat and compacted after treatment. Sample temperatures were varied by means of an external furnace or, for lower sample temperatures, a heating tape surrounding the 28 mm diameter silica discharge tube. The treatment temperatures referred to are nominal values which were measured on the outside of the discharge tube. The methane used was Matheson C.P. grade. Oxygen of 99.9% purity was mixed with the methane for some experiments. Hydrogen of 99.9% purity was used also in some cases.

After plasma treatment the samples, compacted if necessary, were mounted on the specimen stage

of a Varian cylindrical mirror Auger spectrometer. The maximum electron beam energy possible for this spectrometer was 3 kV. The specimen stage could accept up to 3 specimens, which were usually two treated samples and one untreated sample as a reference. The spectrometer vacuum system was evacuated to a pressure of 1×10^{-9} torr, although the system was not baked. A quadrupole mass spectrometer attached to the vacuum system enabled mass spectra of evolved species to be monitored. The Auger spectrometer system was kept relatively clean always by back-filling with pure dry nitrogen and purging with the same gas during specimen exchange. As the specimens were of high surface area, it was usual to allow them to outgas for periods of at least two days and often for as long as one week before measurements were taken. These procedures were followed since it was desired to follow the change of surface composition as a function of temperature. The specimens were heated slowly while records were made of the gases evolved and of the changes in the Auger spectrum. Subsequently the specimens were further heated *in situ* while exposed to low pressures of pure oxygen and Auger spectra again recorded. Finally the specimens were subjected to low energy argon ion bombardment in order to give some estimate of the depth of the surface compositions.

3. Results

3.1. Discharge effects

The phenomena observed for methane discharge sample treatment depended foremost on sample temperature. Variables such as sample position in the discharge tube and discharge intensity did not change the results overall. At lower temperatures, 20 to 100°C, a visible darkening of the discharge tube and samples occurred due to the condensation and polymerization of discharge products [7]. This film could be removed at normal temperature in a time of about 10 min by using a discharge in oxygen. No reduction of the ZnO by atomic hydrogen arising from the dissociation of the methane, was evident at these lower temperatures. Experiments in which atomic hydrogen from a hydrogen glow discharge was passed over the ZnO showed phenomena attributable to reduction only for sample temperatures greater than 300°C. The phenomena which indicate reduction are the evolution of zinc vapour which condenses in the cooler regions of the discharge tube and a

soft light grey surface layer on the ZnO tablets. It was observed that the hydrogen discharge removed the carbonaceous products of the methane discharge for sample temperatures as low as 150 to 200°C. Probably this reaction was the result of a conversion of the deposits to methane by the atomic hydrogen. The removal was not as rapid as observed in an oxygen discharge.

Normally the specimens were treated at a temperature of 400°C for periods of about 15 min. For these conditions, no visible deposition of carbonaceous material on the heated portions of the discharge tube was evident although a heavy dark brown to black film continued to be deposited in the cooler region of the tube under the induction coils. Condensation of zinc was observed on the walls downstream from the heated zone when the specimen was not compacted for treatment. The treated samples had a similar appearance to specimens treated with atomic hydrogen at the same temperature. The surface of the compacted samples was softened. Cleavage of the tablets showed that the darker colour of the surface extended into the tablet to a depth of 10 to 20 μm with quite a sharply defined boundary. Retreatment of some of these specimens in atomic hydrogen at 200°C, lightened the surface colour from dark grey to pale grey.

Treatment of compressed zinc oxide at 400°C in a discharge involving a mixture of 30% of oxygen in methane (by volume) resulted in samples near white in colour. The samples also appeared to be harder than those treated in methane alone. Cleavage again showed a sharply defined surface layer of weak colour change about 10 μm thick. Results with smaller percentages of oxygen were variable, depending very much on sample position relative to the induction coil and upon the discharge intensity. The samples often showed white to grey colour gradation in the direction of gas flow.

3.2. Auger observations and mass spectra

Fig. 1 shows Auger spectra observed for compressed ZnO samples. Notation A refers to the untreated reference specimen, B to specimens treated at 400°C in a methane discharge and C to samples treated at 400°C in a mixture of 30% oxygen in methane. The principal characteristics of the spectra of interest here are the carbon signals. After prolonged evacuation at 20°C these signals were nearly absent in A, moderately strong

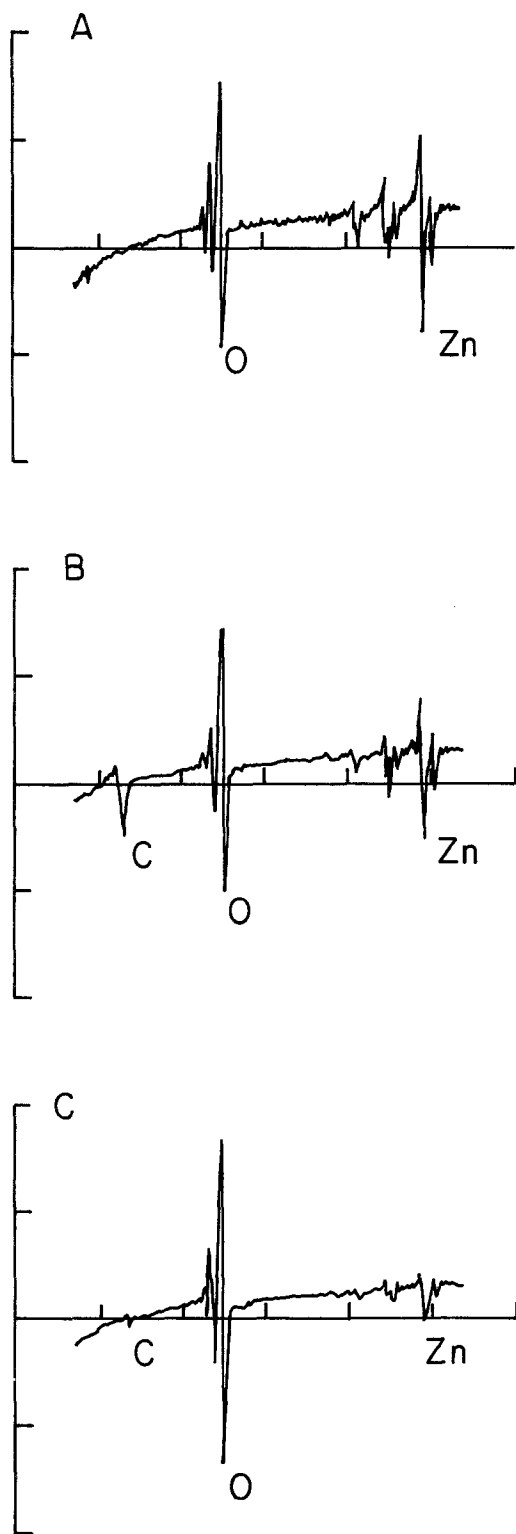


Figure 1 Auger spectra of compressed ZnO powder samples, A untreated reference specimen, B specimen treated at 400° C in a methane discharge, and C specimen treated at 400° C in a discharge of 70% methane and 30% oxygen.

in B and very weak in C. Noticeable also are the ratios of the strengths of the principal zinc and oxygen lines in each sample. The relative strength of the zinc line in C is quite small compared with the same ratio for B which is again a little smaller than for the reference specimen A. Raising the sample temperature to 130° C produced slight increases in the intensities of the carbon signals for samples B and C, probably as the result of removal of physically adsorbed water. Mass spectra obtained during the heating to 130° C showed hydrogen to be the major species evolved followed by water. A temperature of 200° C resulted in further small increases in the carbon signal from samples B and C and a carbon signal was detectable for the first time from sample A. The mass spectra now showed hydrogen remaining as the dominant outgassing species with lesser amounts of water, methane, mass 28 and carbon dioxide. At 300° C sample C showed a marked increase in its carbon signal and an accompanying strong violet fluorescence in the electron beam. The carbon signal for sample B increased only slightly, with violet fluorescence also observed. The carbon signal for A also increased and its fluorescence became violet rather than the whiter colour observed before heating. A relatively strong chlorine line was also now observed in sample A. The mass spectra were temporarily dominated by carbon dioxide in the temperature range from 250 to 300° C, the other species remained as before except that methane replaced water in order of magnitude.

Fig. 2 shows the Auger spectra observed after the specimens had been heated to 400° C. The surface of sample C has darkened markedly and a very strong carbon signal was present. The spectrum of sample B showed little change compared with 300° C. The carbon peak for the reference specimen A had increased to a level comparable with sample B but no colour change was evident. The degassing species present at this juncture were hydrogen, methane, water, mass 28 and mass 44 in order of mass spectrum peak height. The chlorine Auger peak for the reference specimen had become very strong. This impurity probably arose from the method of manufacture of ZnO powder.

The samples were next exposed to a pressure of 1 torr of oxygen and then heated to 400° C for 10 min, cooled to 150° C, evacuated and allowed to cool further to 20° C. This treatment produced the Auger spectra shown in Fig. 3.

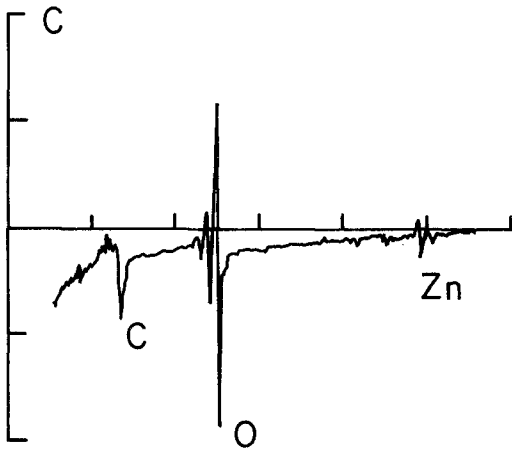
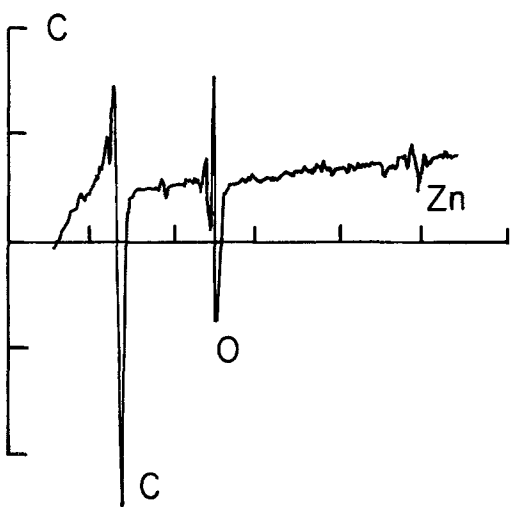
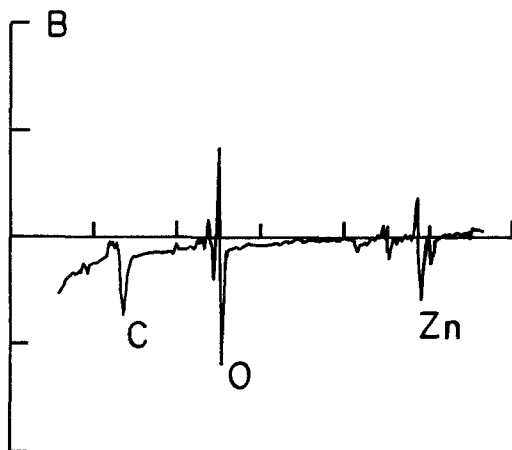
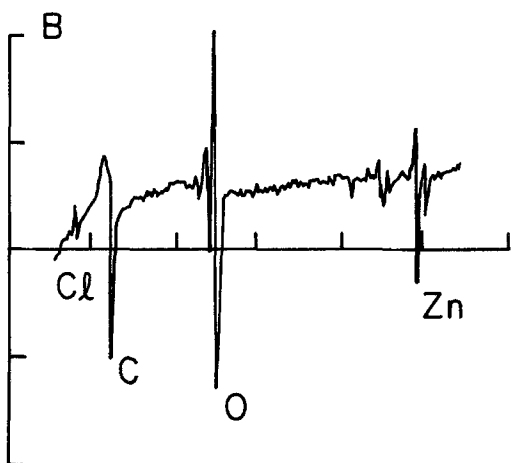
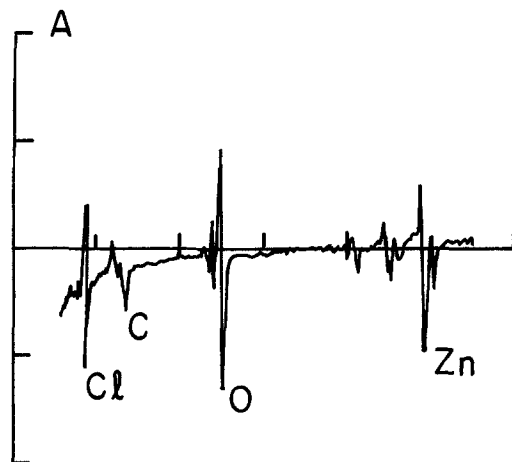
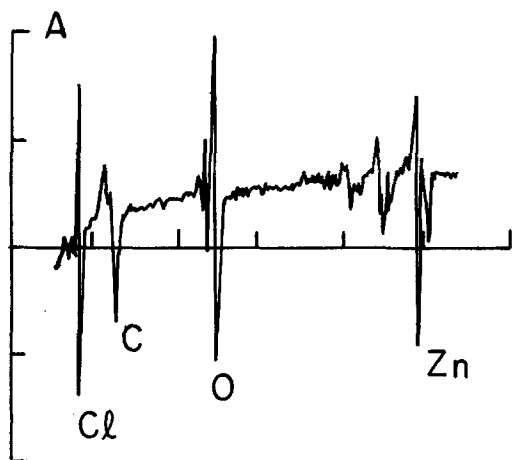


Figure 2 Auger spectra of the specimens as in Fig. 1 after they had been heated to 400° C in vacuum.

Figure 3 Auger spectra of the specimens as in Fig. 1 after they had been heated in 1 torr oxygen to 400° C for 10 min, cooled to 150° C, evacuated and allowed to cool to 20° C.

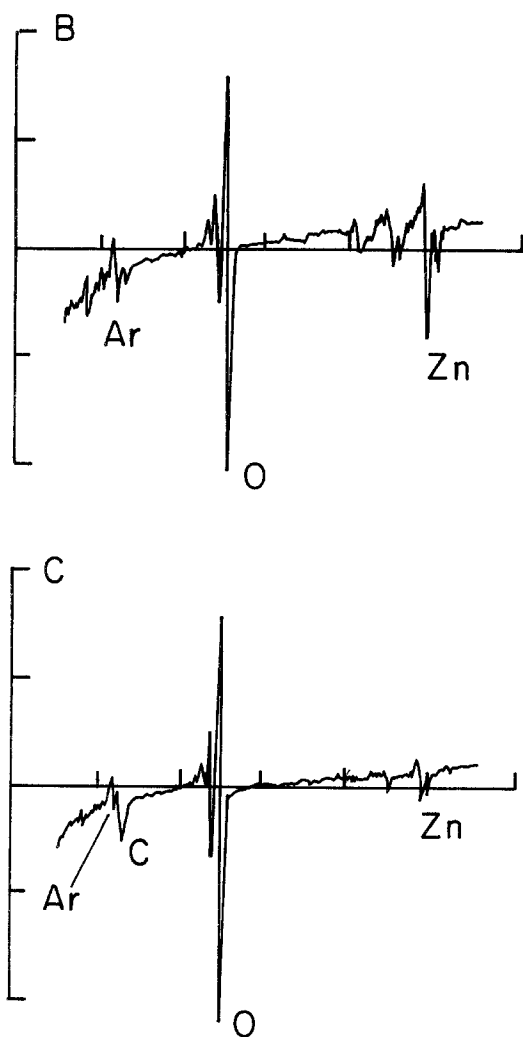


Figure 4 Auger spectra of specimens B and C of Fig. 1 after they had been bombarded with argon ions of 600 eV energy, current of 10 μ A for 15 min.

Marked changes occurred in the characteristics of sample C; the electron beam induced fluorescence changed from violet to white, the sample surface colour also changed to white and a large decrease in the Auger carbon peak relative strength occurred. The other samples showed less decrease

in their carbon Auger signals. The surface colour of sample B changed to white from pale grey. Re-heating the samples to 400°C in vacuum restored the strong violet fluorescence to specimen C. Its surface darkened and the Auger spectrum once more showed a very strong carbon peak. Sample B also resumed a slightly darkened appearance, its Auger carbon peak increased slightly and violet fluorescence was observed again. The characteristic reference sample A remained virtually unchanged. Hydrogen and carbon dioxide were the prominent outgassing peaks in the mass spectra during this heat treatment.

Sample examination concluded with argon ion bombardment (600 eV, 10 μ A, 15 min) of samples B and C. As the result of this treatment sample B resumed its original grey colour and sample C its original white colour. The Auger spectra of both samples now showed greatly reduced carbon peaks (Fig. 4). Re-heating to 400°C in vacuum did not cause sample C to regain a strong carbon signal on this occasion.

The Auger observations of the variation of the carbon signal strength during the sequence of sample treatments described are summarized in Table I in terms of the ratio of the peak height to the principal peak in the oxygen spectrum.

A striking characteristic of many samples which were treated in the oxygen-methane mixture at 400°C, was the very low intensity of the zinc Auger peak. The persistence of this anomaly despite heat treatment and ion bombardment suggested the effect was structural in origin.

4. Discussion

The observations of principal interest in the present study are those associated with the treatment of ZnO in methane-oxygen discharge mixtures. The outstanding characteristic of this treatment is the very strong Auger carbon peak produced by heating the treated samples to 400°C in vacuum. Nearly all the carbon contributing to this Auger signal must be near the surface of the

TABLE I

Discharge treatment	Ratio carbon to oxygen peak heights						
	Initial evacuation	Heated to 130° C	Heated to 220° C	Heated to 300° C	Heated to 400° C	Heated to 400° C in O ₂	Heated to 400° C in vacuum
None (ref. sample)	—	—	0.16	0.28	0.48	0.3	0.32
CH ₄	0.25	0.3	0.3	0.56	0.57	0.35	0.48
CH ₄ /30% O ₂	0.04	0.12	0.8	0.52	1.77	0.24	0.9

sample if the ready reduction of the carbon signal by heating in oxygen is to be easily explained (Table I).

The recovery in the Auger carbon signal strength produced by evacuation of the sample at 400°C after oxygen treatment (Table I) points to some transport mechanism of carbon to the external surface from the interior of the sample. The same mechanism is likely to be responsible for the rise in the carbon signal during the initial heating of the specimen in vacuum. An alternative hypothesis in this latter case is that of removal of adsorbed oxygen or water vapour which overlay the carbon. This hypothesis is not supported by the observations of the gases evolved during the initial heating. That is, the majority of the water vapour is evolved below 200°C before the rapid increase of carbon signal and there is very little accompanying oxygen evolution.

The apparent source of carbon in the samples must diffuse into the sample relatively rapidly during the time of the discharge treatment at 400°C. In this treatment the depth of the sample visibly affected by the discharge amounted to approximately 10 μm. Accepting this distance as the extent of carbon penetration (x) into the sample and given a treatment time of approximately 1000 sec, an overall diffusion rate, both for surface diffusion over the individual grains and bulk diffusion, can be calculated from the random walk relation, $x^2 = 2Dt$ [8], of $D = 10^{-9}$ cm² sec. This value may be compared with the diffusion rates at 400°C measured for interstitial zinc and hydrogen in single crystal ZnO of about 10⁻⁷ and

10⁻⁸ cm² sec, respectively [9, 10]. No conclusions about the role of hydrogen in the present study is possible.

The Auger carbon signal characteristics of the other sample types (Table I) are generally similar, apart from signal strength, to those observed with the methane-oxygen treatment. There did not appear to be a significant effect on the untreated ZnO of carbonate formation [11] due to exposure to the atmosphere. The origin of the carbon impurity in the untreated material is not known.

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