Microstructure of zirconia films deposited with ion assistance

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Zirconia films were deposited in vacuum from an electron-beam hearth with simultaneous ion bombardment from a Kaufman source. The effects of argon, oxygen and nitrogen ions were investigated, together with those of temperature and substrate type. For amorphous substrates, without ions, X-ray and electron diffraction showed that amorphous films were produced at room temperature. Deposition on to 300° C amorphous substrates produced the monoclinic form. Ion assistance converted the structure to cubic. It was found that deposition on to KCl (1 0 0) substrates also produced the cubic form at elevated temperatures, with or without ions. High-resolution microscopy showed that these films were crystallographically oriented with either $\langle 1\,0\,0 \rangle$ or $\langle 1\,1\,0 \rangle$ normal to the KCl substrate. The Raman spectra of films on fused silica substrates were correlated with the X-ray diffraction scans and the conditions under which the Raman spectrum could be used as a reliable indicator of microstructure were found.

1. Introduction

The microstructure of optical thin films influences their physical properties and largely determines the stability and durability of optical elements incorporating thin films. Void spaces are often present, lowering the refractive index from the bulk value and rendering the film susceptible to penetration by atmospheric water vapour. The use of ion bombardment during film deposition has been shown to have beneficial effects in many cases, leading to densification by elimination of these void spaces (see, for example, Martin *et al.* [1]). The modification by ions of the columnar growth mode which leads to the void spaces has been well documented [1]. Less well studied, however, is the effect of ions on the microstructure at the atomic level. The effect of ions on the atomic arrangement is of special importance in materials which show a variety of crystallographic structures under various conditions of temperature and pressure. The latter aspect of ion-assisted deposition is addressed in this study using zirconium dioxide (zirconia, ZrO_2) as an example.

ZrO_2 shows three principal crystalline structures. The monoclinic form, baddeleyite, is the stable form at room temperature. This form has space group $P2_1/C$ with $a = 0.521$ nm, $b = 0.526$ nm, and $c = 0.537$ nm with $\beta = 80°\,32'$ [2–4]. A tetragonal form is produced by heating to about 1100° C, having space group $P4_2/nmc$ with $a = 0.507$ nm and $c/a = 1.016$ [5]. Further heating to 2300° C produces a transformation to a cubic form with the fluorite structure, space group F m3m and cell parameter a ranging from 0.508 to 0.521 nm. The cubic form can be stabilized at room temperature by the addition of up to 10 mol % MgO,

CaO or Y_2O_3. The addition of CaO or Y_2O_3 somewhat enlarges the cell parameter to about 0.513 nm [6]. The tetragonal form is present in partially stabilized zirconia where it leads to the useful mechanical properties of these materials [7].

In a previous study of zirconia thin films [8], it was deduced from X-ray diffraction scans that for films deposited at room temperature on to glass substrates, ion assistance with argon or oxygen ions at current densities above $0.05\,A\,m^{-2}$ converted the normally amorphous structure into the cubic form. For glass substrates heated to 300° C, X-ray diffraction scans showed that the films had a monoclinic structure which was substantially converted to the cubic form by argon- or oxygen-ion assistance. In this study we confirm these conclusions by applying, in addition to X-ray diffraction, the techniques of electron microscopy and diffraction and Raman spectroscopy, and we determine the effect of the substrate by comparing films deposited on amorphous substrates (glass, fused silica or amorphous carbon) with those prepared on the cleaved (1 0 0) face of KCl single crystals.

2. Electron microscopy and diffraction

Films of ZrO_2 in the thickness range 20 to 40 nm were prepared from monoclinic source material by evaporation using an electron-beam system. Argon-, oxygen- or nitrogen-ion beams from a Kaufman ion source were used to assist the deposition. The base vacuum was 10^{-3} Pa increasing to 10^{-2} Pa during ion assistance. Details of the deposition system are provided in an earlier paper [8]. The substrates were either thin amorphous carbon films supported on electron microscope copper grids or crystals of KCl
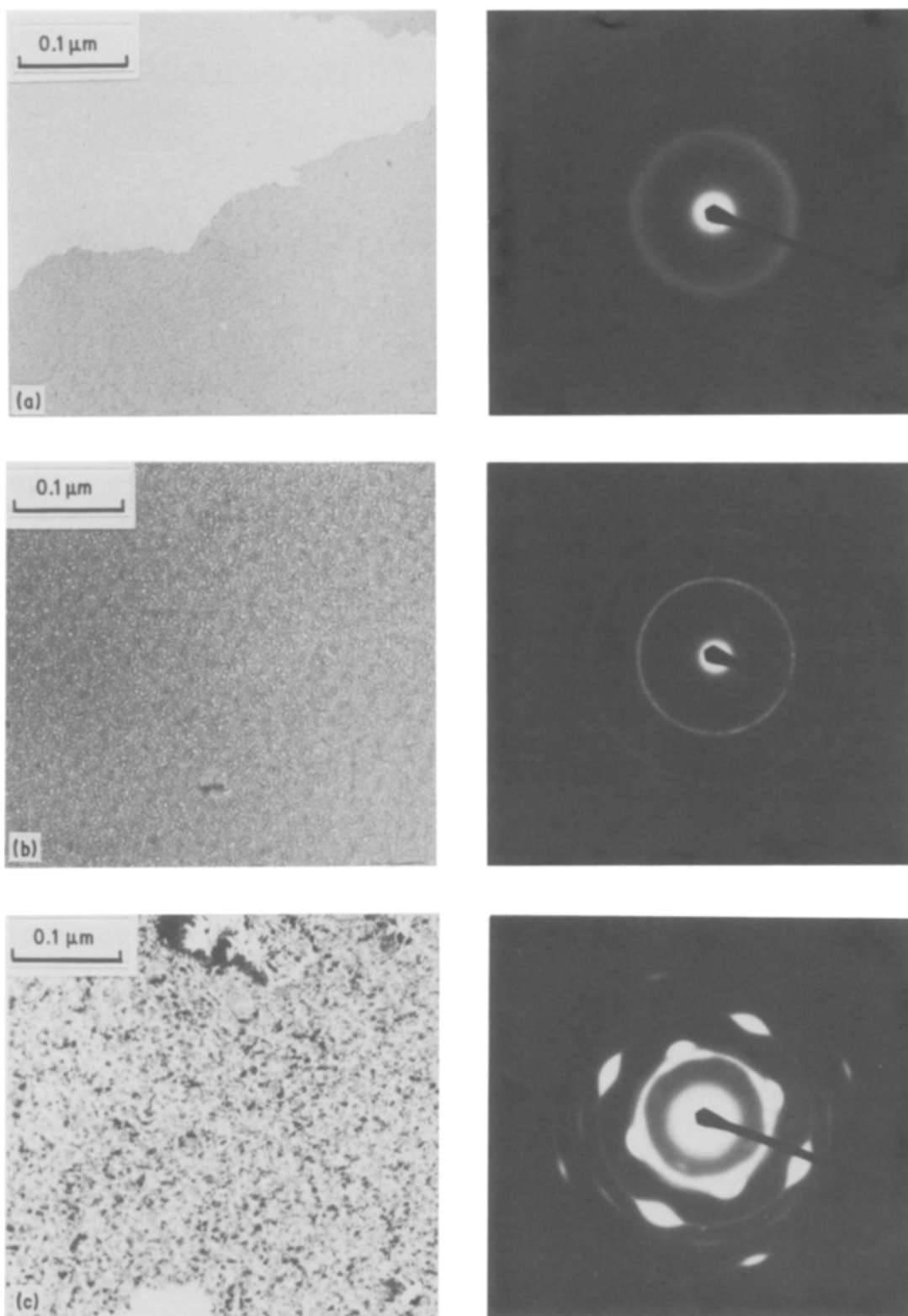
Figure 1 Transmission electron microscope images and corresponding diffraction patterns of ZrO_2 thin films. (a) A film deposited on to KCl at room temperature. The film is fine-grained and the diffraction pattern shows it to be amorphous. (b) A film prepared on a KCl substrate at room temperature with oxygen-ion assistance. The film has a microcrystalline structure consisting of the cubic phase. (c) A film prepared on a KCl substrate at 300° C with argon-ion assistance. The film shows 5 nm crystals with strong preferred orientation.

cleaved along (1 0 0) faces. For electron microscopy, films prepared on amorphous carbon were examined as-prepared, while films prepared on KCl were floated off in distilled water and transferred to grids. The substrate temperature was either room temperature or 300° C.

Deposition at room temperature without ion assistance invariably gave amorphous films and the struc-

ture was not influenced by the type of substrate. An example is shown in Fig. 1a. Ion assistance of films prepared at room temperature induced some crystallinity for ion currents above about $0.05 \, A \, m^{-2}$, with some amorphous phase remaining. An example is shown in Fig. 1b which was prepared on a KCl substrate at room temperature with nitrogen-ion assistance. The film shows a fine-grained microstructure
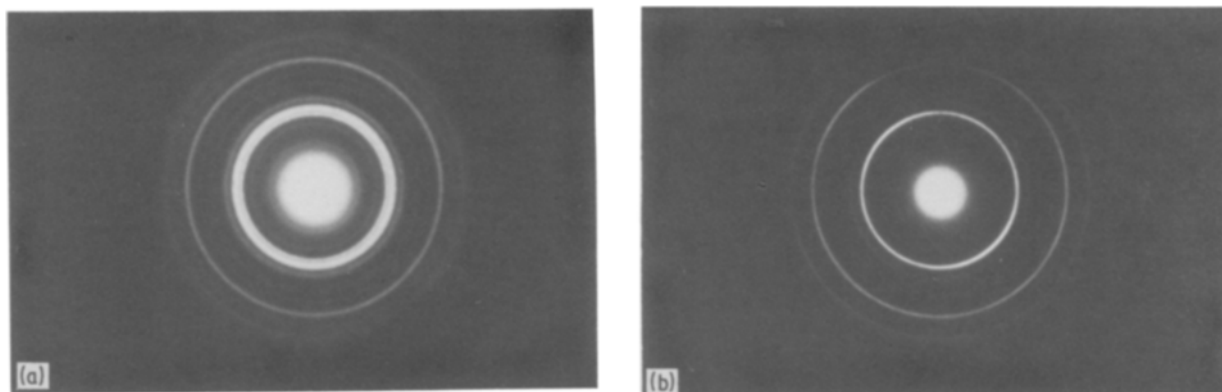
Figure 2 Electron diffraction patterns of ZrO_2 films prepared on amorphous carbon support films. (a) A monoclinic film prepared on a substrate at 300° C. (b) A cubic film grown under the same conditions as (a) except for argon-ion assistance. This film shows a cubic structure.

with a cubic diffraction pattern. The electron beam (100 kV) induced crystal growth so that the crystalline structure became more clearly defined with time under the beam. Films prepared with oxygen- and argon-ion assistance at room temperature also showed mixed crystalline and amorphous structure.

Heating of the substrate to 300° C during deposition had an effect which was dependent on the type of substrate. For KCl substrates, the structure was crystalline with a grain size of 5 nm, as shown in Fig. 1c. The corresponding diffraction pattern shows that the crystals have a cubic diffraction pattern and show strong preferred orientation, a result of some epitaxy on the KCl (1 0 0) substrate. The effect of argon-ion assistance on both the image and the diffraction pattern was not significant. We deduce that the atom mobility on the heated KCl substrate is sufficient to allow epitaxy to occur. The cubic symmetry of the substrate then stabilizes the cubic structure. Ion assistance may provide some additional mobility and conversion to the cubic form but the substrate effect is dominant and the overall result is not changed.

For heated amorphous substrates the effect of ion assistance is important, as it was for both substrates at room temperature. Heating an amorphous substrate without ion assistance invariably produces a crystalline monoclinic structure. Fig. 2a shows the diffraction pattern of such a film prepared on an amorphous carbon support film, showing the large number of rings characteristic of the monoclinic phase. Fig. 2b shows the diffraction pattern of a film grown under identical conditions to that of Fig. 2a, but with argon-ion assistance at about 0.05 A m^{-2}. The pattern of Fig. 2b was indexed as cubic ZrO_2 using a platinum calibration (see Table I). We deduce that the formation of the cubic phase under ion assistance both at room temperature and at 300° C is a consequence of the strong temperature and pressure spikes following ion impact. These spikes are rapidly quenched so that the cubic form, stable at high temperatures and pressures, is frozen in.

Selected-area diffraction patterns were digitized by scanning them over the entrance aperture of an electron energy loss spectrometer set to receive elastic scattering only. The cubic diffraction pattern corresponding to Fig. 1c is shown in Fig. 3a. The main peaks were indexed according to the cubic structure as

shown in Table I. There are, however, some weak peaks which could not be indexed according to the cubic fluorite structure. One of these probably results from traces of the tetragonal structure while the other occurs at the normally forbidden (1 0 0) positions and may be due to the relaxation of the extinction rule for small crystallites. Observation of the lattice parameter values of Table I suggests that cubic material formed on KCl substrates has a smaller parameter than that formed by ion bombardment on an amorphous substrate.

The monoclinic diffraction pattern corresponding to Fig. 2a is shown in Fig. 3b. Most of the lines of the monoclinic baddeleyite structure which are present in the X-ray diffraction pattern of the baddeleyite source material are also present in Fig. 3b, as shown in Table I, confirming the monclinic structure.

Further investigation of the cubic structure was carried out by high-resolution microscopy using a Philips EM430 microscope operating at a resolution of 0.18 nm at 300 kV. A 20 nm film grown at 300° C with argon-ion assistance on a KCl substrate was
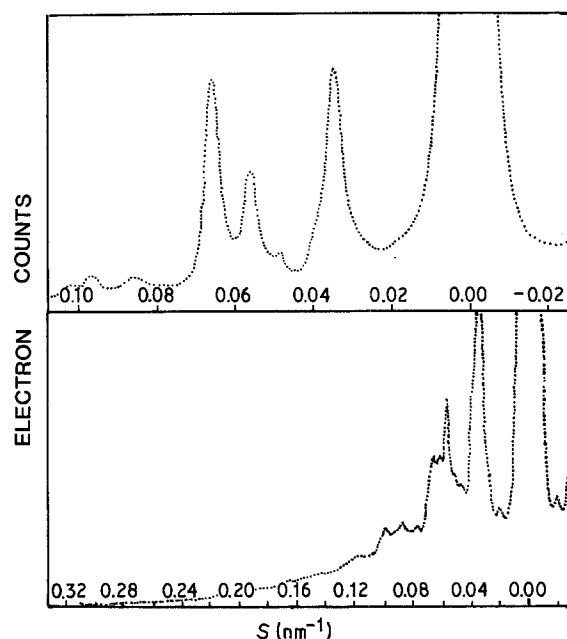

Figure 3 Electron diffraction patterns obtained by means of an electron energy loss spectrometer set to receive elastic scattering. The upper plot shows the cubic pattern of Fig. 1c while the lower plot shows the monoclinic pattern of Fig. 2a; $s = 2 \sin \theta/\lambda$.

TABLE I The values of $s = 2 \sin \theta/\lambda \, (\text{nm}^{-1})$ for diffraction maxima in X-ray and electron diffraction scans for ZrO_2 bulk materials and films

(a) Materials showing cubic structure, giving indices, and cell parameter, a (RT = room temperature)

hkl	Y$_2$O$_3$-stabilized powder (X-ray)	Film on RT glass + Ar ions (X-ray)	Film on RT glass + O$_2$ ions (X-ray)	Film on hot a–C + Ar ions (electron)	Film on hot KCl no ions (electron)	Film on hot KCl + Ar ions (electron)	Film on hot KCl + O$_2$ ions (electron)
1 0 0*						1.99*	
1 1 1	3.36	3.30	3.33	3.30	3.45	3.42	3.43
2 0 0	3.90	3.79		3.90	3.92	3.98	3.92
						4.81*	
2 2 0	5.51	5.43	5.51	5.47	5.55	5.56	5.60
3 1 1	6.46			6.24	6.60	6.51	6.55
2 2 2	6.73						
4 0 0	7.79						
3 3 1	8.47						
4 2 0	8.70				8.85	8.54	8.69
4 2 2						9.63	9.74
5 1 1, 3 3 3						10.45	
a (nm)	0.514	0.524	0.515	0.521 ± 0.009	0.505 ± 0.005	0.508 ± 0.005	0.506 ± 0.005

*Not indexable as cubic ZrO_2.

(b) Materials showing monoclinic structure, with approximate relative intensities in brackets (RT = room temperature)

Baddeleyite powder (X-ray)	Film on hot glass, no ions (X-ray)	Film on hot a–C no ions (electron)
		2.0 (0.5)
3.17 (10)	3.17 (10)	3.1 (1)
3.53 (8)	3.53 (3)	3.5 (10)
3.82 (2.5)		
3.93 (1.5)		3.9 (2)
4.54 (2.0)		4.6 (0.5)
4.99 (1.0)		5.1 (0.5)
5.41 (2.5)		
5.53 (2.2)	5.53 (0.2)	5.5 (0.5)
5.89 (1.0)	5.89 (0.2)	5.8 (0.3)
6.04 (1.5)		
6.22 (1.0)		6.2 (0.5)
6.66 (1.2)		6.6 (0.2)
		7.9 (0.2)
		8.9 (0.2)

used. The strong preferred orientation is visible in Fig. 4 in which lattice images are clearly visible. Cubic crytallites with $\langle 1\,0\,0 \rangle$ and $\langle 1\,1\,0 \rangle$ normal to the substrate were both observed. Diffraction patterns corresponding to each orientation are shown in Fig. 3, together with a region of the specimen containing crystallites in the corresponding orientaton. The relative amounts of the two orientations varied across the specimen.

Optical diffractograms were obtained from individual grains in the high-resolution electron micrographs, using an optical bench. These clearly showed the cubic structure of individual crystallites with both $\langle 1\,0\,0 \rangle$ and $\langle 1\,1\,0 \rangle$ orientation.

3. Raman spectroscopy and X-ray diffraction

Previous studies of the Raman spectrum of ZrO_2 films (e.g. [9]) have, in our opinion, not been conclusive in providing unambiguous evidence of the presence of a given phase because of the close coincidence in the Raman frequencies of the three phases [10] and the possibility of preferred orientation in the films. Conse-

quently, the X-ray diffraction pattern of each specimen was taken in addition to the Raman spectrum so that a correlation could be made between the results of the two techniques.

For Raman spectroscopy, films are prepared on fused silica substrates. The line at 514.5 nm from an argon-ion laser was used as the exciting radiation. The specimens were mounted at 45° to the incident beam and spectra were collected in the frequency range 200 to 1000 cm^{-1}. Selected spectra are shown in Fig. 5 with corresponding X-ray diffraction patterns.

To provide reference spectra of cubic material, a specimen of powdered cubic ZrO_2 stabilized with 4 mol % Y_2O_3 was used. The positions and strengths of the Raman bands are shown in Table II. It has been pointed out by Phillippi and Mazdiyasni [10] that the pure cubic form in a metastable state should show only one Raman active vibrational mode at 490 cm^{-1}. The presence of additional Raman bands is due to the presence of stabilizing oxides inducing lattice strain [11]. Because of many close coincidences of these induced bands with frequencies of the tetragonal and monoclinic phases, the use of them as indicators of the presence of the cubic phase is difficult. Furthermore, the agreement between authors on the values of the frequencies as given in Table II is not good. This may be because the strength and position of the bands are strongly influenced by the type and degree of lattice strain in various stabilized cubic specimens. Consequently, the best evidence for the existence of the cubic phase is provided by diffraction. It is worth noting, however, that the observed bands in the cubic film shown in Table IIa at 603 and 251 cm^{-1} coincide reasonably well with the two strong bands in CaO-stabilized cubic zirconia [11]. These two bands, therefore, provide indicators in the Raman spectrum of the presence of the cubic phase in thin film form.

The situation for the monoclinic phase is much more satisfactory. Good agreement in the position and intensities is found between the monoclinic bulk specimen and the literature values [10] and between both of these and a monoclinic thin film prepared on

TABLE II Raman spectra of various forms of ZrO_2. Frequencies of Raman lines are given in cm^{-1} (vw = very weak, w = weak, m = medium, s = strong, b = broad)

(a) Cubic forms

Metastable cubic	Y_2O_3-stabilized [10]	CaO-stabilized [11]	Y_2O_3-stabilized (this work)	Film on hot glass + Ar ions (this work)
			956 (s)	
			850 (w, b)	
		637 (w)		700 (m)
	625 (m, b)	606 (s, b)	614 (m)	603 (m)
490 (w, b)	480 (w, b)	465 (w)	419 (w)	
			393 (w)	
			378 (m)	
			351 (m)	
		317 (w)	319 (w)	
	250 (w, b)	259 (s)	285 (m)	251 (m)
	150 (w, b)	147 (m)		

(b) Monoclinic forms

Baddeleyite [10]	Baddeleyite (this work)	Film on hot glass no ions (this work)
638 (m)	632 (m)	638 (m)
617 (m)	610 (m)	619 (m)
559 (w)	559 (w)	557 (w)
538 (w)	521 (m)	
502 (w)	500 (w)	502 (w)
476 (s)	470 (s)	476 (s)
382 (m)	373 (m)	382 (m)
337 (m)		347 (w)
		334 (w)
307 (w)		308 (w)
223 (w)		218 (w)
192 (s)		
180 (s)		
104 (m)		

a hot glass substrate with no ion assistance. The Raman spectrum, therefore, provides good evidence for the existence of the monclinic phase provided that a sufficient number of the monoclinic bands are identified and matched in frequency and intensity. Because of the close coincidence of most bands with observed cubic bands, it is not possible to draw any conclusions from the presence of one or two of these bands.

4. Conclusions

The principal conclusions of this work are

1. The cubic form of zirconia can be prepared in thin-film form either by ion-assisted deposition on amorphous substrates or by growth on a KCl (1 0 0) substrate at elevated temperature.
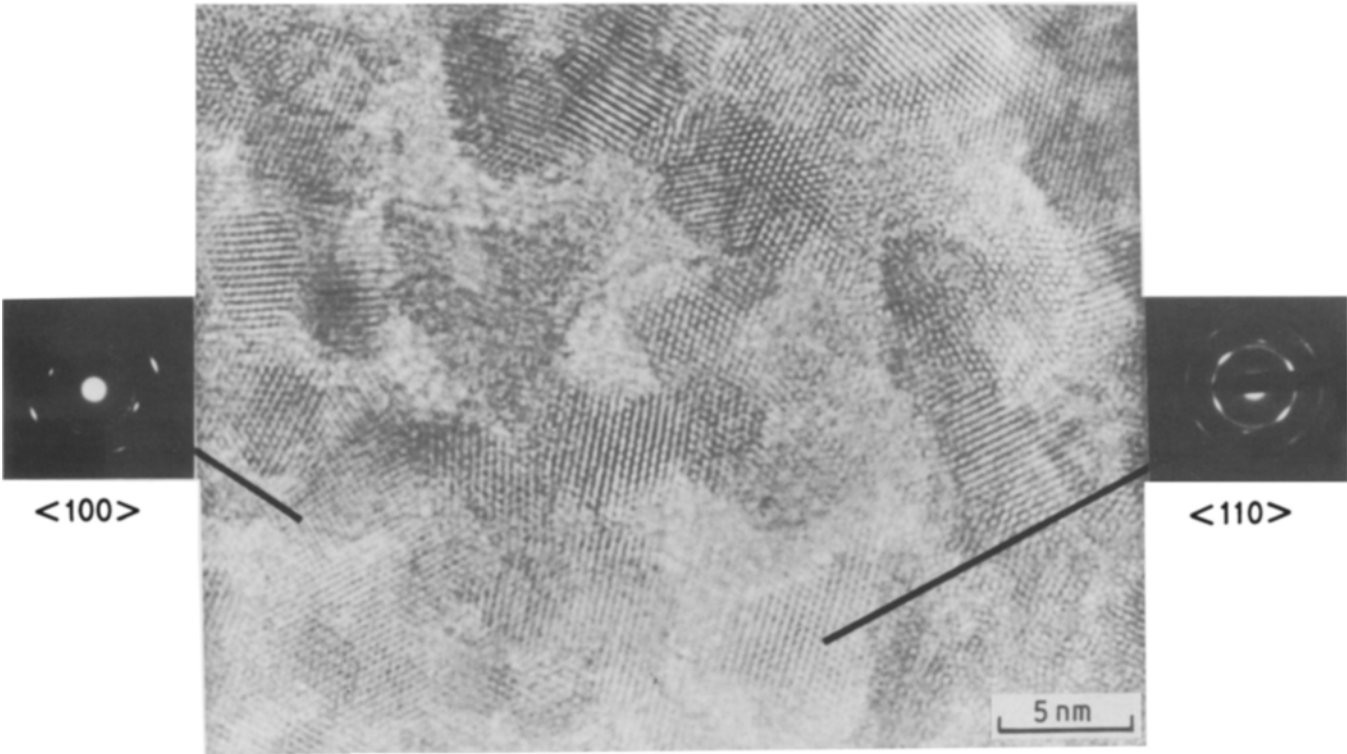

Figure 4 A high resolution micrograph of the film of Fig. 1c showing 5 nm crystallites with strong preferred orientation. Crystallites showing $\langle 1\,0\,0 \rangle$ normal to the substrate and $\langle 1\,1\,0 \rangle$ normal to the substrate are indicated with diffraction patterns from regions in which the particular orientation is predominant.
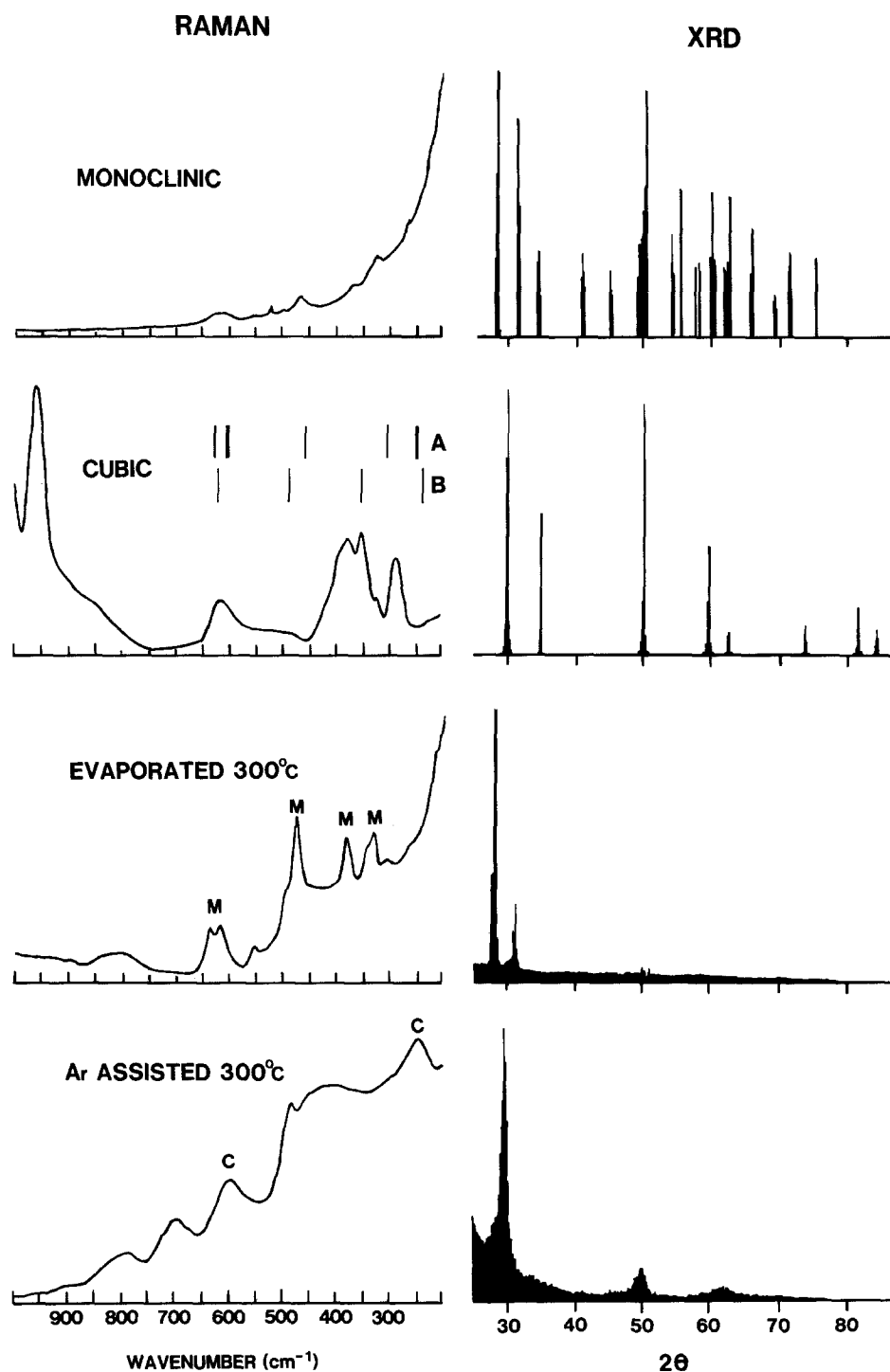
Figure 5 Raman spectra and corresponding X-ray diffraction scans taken with CuKα radiation. From top to bottom the specimens are monoclinic bulk material; Y_2O_3-stabilized cubic bulk material; a thin film prepared on a 300° C fused silica substrate; a thin film prepared on a 300° C fused silica substrate with argon-ion assistance. M indicates Raman bands characteristic of the monoclinic phase and C indicates Raman bands characteristic of the cubic phase. A and B indicate spectra obtained from stabilized cubic specimens in [11] and [10], respectively.

2. In the case of KCl (1 0 0) substrates, strong preferred orientation is produced with ⟨1 0 0⟩ or ⟨1 1 0⟩ directions in the ZrO_2 normal to the substrate.

3. The Raman spectrum provides an indicator of the presence of monoclinic and cubic phases provided that care is taken to match both frequencies and intensities of the Raman bands.

Acknowledgements

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