
Synthesis and characterisation of nitrogen-doped ZnO thin films

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Abstract: Nitrogen doped ZnO thin films were prepared using a DC-Magnetron sputtering technique. The samples were investigated using X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD). XPS revealed the presence of nitrogen in the films prepared under high oxygen to nitrogen ratio $N/O \geq 5/1$. One N 1s peak located at 397 eV binding energy (BE) was assigned to atomic nitrogen. The other located at a BE of 399 eV was assigned to N due to formation of oxynitride. The XRD spectrum of the samples prepared under N/O ratio $\geq 1/5$ showed a single peak at $2\theta \sim 33.6^\circ$ assigned to ZnO (002) plane indicating a strong texture along the c-axis. Both peaks were shifted toward lower angles, as compared to pure ZnO film, indicating an expansion of the unit cell as a result of the insertion of nitrogen in the lattice. The nanostructure of the films was investigated by atomic force microscopy.

Keywords: nitrogen doped zinc oxide; ZnO thin films; DC magnetron; nanotechnology.

Reference to this paper should be made as follows: Mekki, A., Tabet, N. and Hezam, M. (2009) 'Synthesis and characterisation of nitrogen-doped ZnO thin films', *Int. J. Nano and Biomaterials*, Vol. 2, Nos. 1/2/3/4/5, pp.216–225.

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1 Introduction

Nanostructures of wide band gap semiconductors such as ZnO are of particular interest in short wavelength light emitting and field emission devices and many other fields of applications. Many approaches have been used to prepare nanorods or nanowires, but the exploration of novel and simple method is still a challenging research area. The bandgap of bulk ZnO is reported to be 3.37 eV with a 60 meV binding energy (BE) of the free exciton which permits excitonic emission at room temperature (Cho et al., 1999; Wang et al., 2003). This large band-gap is suitable for the use of ZnO to collect high-energy photons (UV light) (Bae et al., 2003). ZnO transparency in the visible range exceeds 80% beyond the wavelength of the absorption edge (Sernelius et al., 1988; Lee et al., 2004; Oh et al., 2005). These attractive physical properties give ZnO potential applications in optoelectronics (Cho et al., 1999; Wang et al., 2003; Fan et al., 2004; Bae et al., 2003; Sernelius et al., 1988, Lee et al., 2004; Oh et al., 2005; Zamfirescu et al., 2002; Yan et al., 2001). ZnO nanorods with diameters of 20–100 nm, are currently obtained by various methods (Park et al., 2002; Wang et al., 2005b; Banerjee et al., 2005; Yang and Gao, 2005; Wang et al., 2005a; Fan et al., 2004). These nanorods can be prepared simply by heating metallic zinc at temperatures above the melting point of zinc (419°C) (Dang et al., 2003; Avalle et al., 1992; Meng et al., 1994; Tabet et al., 2007b). Several p-type dopants, including nitrogen (N), phosphorus (P) and arsenic (As) have been used to prepare p-type ZnO thin films. Among them, the most promising candidate seems to be N. A review of literature shows that significant efforts have been made in the N doping of ZnO thin films by various techniques (Minegishi et al., 1997; Guo et al., 2002; Look et al., 2002; Li et al., 2003b; Li et al., 2003a; Rommeluere et al., 2003; Meyer et al., 2004; Bian et al., 2004). However, the growth of p-type ZnO films is still a subject of intensive investigation. DC magnetron sputtering is one of the techniques used in doping ZnO thin films with nitrogen. In the present investigation, we report on the properties of ZnO thin films prepared at room temperature by DC magnetron sputtering under N-rich atmosphere.

2 Experimental details

ZnO thin films were deposited at room temperature by the DC reactive magnetron sputtering on ordinary optical microscope glass slides that were cut into a size of 1 x 1 cm². The slides were cleaned with acetone before thin film deposition. A disc of pure (99.999%) metallic zinc of 5 cm diameter was used as a target. The

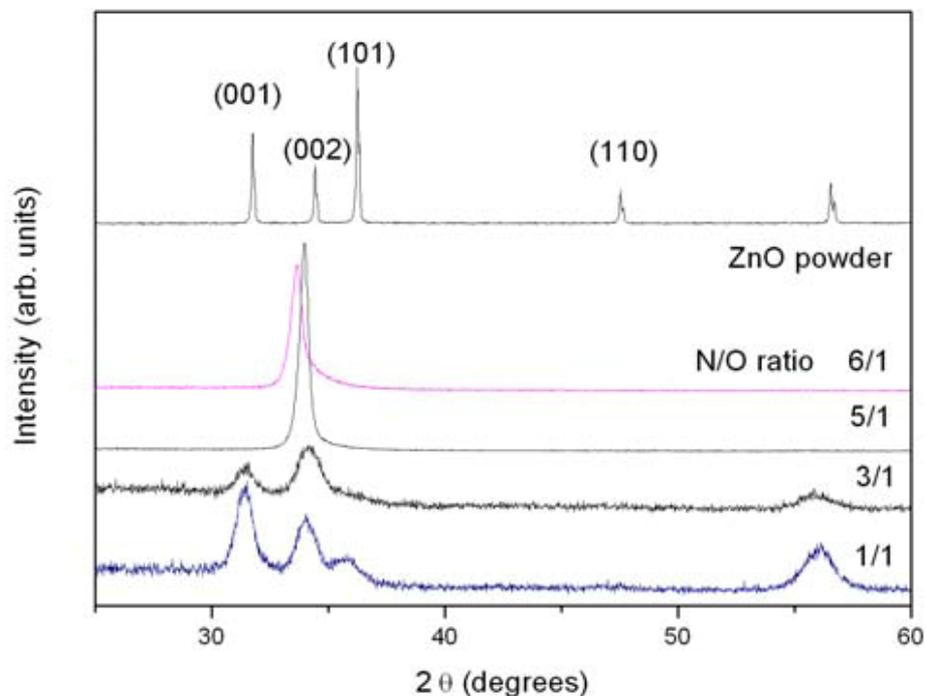
target-to-substrate distance was about 3 cm. The sputtering chamber was pumped down to about 1×10^{-3} Pa. Then a mixture of high purity oxygen and nitrogen was introduced in the sputtering chamber. A gas flow meter was used to control the flow of gas in the preparation chamber. The working pressure during film growth was set at 1×10^{-2} Torr.

Before deposition, the zinc target was pre-sputtered for about five minutes with a shutter covering the substrate in order to remove the surface oxide layer. Sputtering deposition was performed under a voltage of 500V and a current 70mA. The sputtering time was about 15 minutes.

The structure of the thin films was studied using a Shimadzu XRD-6000 X-ray diffractometer using a Cu anode (K_{α} , $\lambda = 1.5418\text{\AA}$). X-ray photoelectron spectroscopy (XPS) of the type VG-ESCALAB MKII equipped with a dual X-ray source (Al/Mg) was used to estimate the atomic composition of the films, while the morphology of the films was investigated using AFM instrument type INNOVA-Veeco.

3 Results and discussion

All the films investigated were prepared under the same experimental conditions except for the mixing ratio of N/O gases. The thin film samples were therefore labelled based on their mixing ratio. The structure, composition and morphology of the films were characterised by XPS, X-ray diffraction (XRD) and AFM. Figure 1 shows the θ - 2θ XRD pattern obtained from the as grown films. The spectrum labelled 1/1 was prepared under nitrogen to oxygen ratio of 1/1. As seen from the figure, four peaks are present at 2θ angles of 31.4° , 34.04° , 35.76° and 55.9° corresponding to (100), (002), (101) and (110) planes of pure ZnO, respectively. Film 2 was prepared under O/N ratio of 1/3 and labelled in the figure as 1/3. The spectrum looks similar to that of film 1 except for the absence of the third peak at $2\theta \sim 35.8^{\circ}$ corresponding to reflections from (101) direction. In film 3, which was prepared under O/N ratio of 1/5, we note the presence of only the (002) Bragg reflection at $2\theta = 33.98^{\circ}$ which indicates that this film is fully c-axis oriented. The last film in the series, prepared under O/N ratio of 1/6, also shows preferential orientation along the c-axis with a diffraction angle $2\theta = 33.64^{\circ}$. For comparison purposes, we list here 2θ angles for pure ZnO powder for (100), (002), (101), and (110) as 31.75° , 34.43° , 36.25° , and 56.57° , respectively. We notice that introducing N into the ZnO thin film induces a decrease in the 2θ angle for the (002) direction from 34.43° – 33.64° . The values of the c lattice parameter extracted from the XRD data are reported in Table 1. As seen from the table, the c parameter increases from 0.2729 nm for ZnO powder to 0.2783 nm for an N/O ratio equal to 6/1, that is an increase of about 2% in the c parameter. The full width at half maximum (FWHM) for the (002) peak was found to decrease from 1.17° – 0.46° with increase in N content in the film. This indicates that the grain size increases with increase in N content in the film. Using Sherrer's relation between the grain diameter D and the FWHM, that is $D = \frac{\lambda}{FWHM \times \cos \theta}$, we can estimate the average grain diameter for the films. The results are reported in Table 1. As seen from the table, D increases from 8.86 nm to 31.3 nm. Introducing N into the ZnO structure seems to induce an increase in the grain size.

Figure 1 XRD pattern of the as grown films (see online version for colours)

Note: The XRD pattern of the ZnO powder is also shown as reference.

Table 1 XRD data for the peak due to the (002) direction and the grain diameter D estimated from Sherrer's formula

N/O	$2\theta(002)$ (degrees)	$FWHM$ (degrees)	D (nm)	c (nm)
ZnO powder	34.39	0.165		0.2729
1/1	34.17	1.17	8.86	0.2745
3/1	34.04	1.05	10.4	0.2754
5/1	33.96	0.59	21.7	0.2760
6/1	33.63	0.46	31.3	0.2783

Note: The last column represents the c lattice parameter.

XPS was used to record the N 1s, O 1s and Zn 2p core level spectra for the four films analysed. Figure 2 shows the N 1s core level spectra for the N-doped films. It is clear that for films with N/O ratio of 1/1 and 3/1, XPS did not detect any nitrogen content in the films. This might be due to the fact that the concentration of nitrogen in these two films is lower than the detection limit of the XPS technique. For the films labelled 5/1 and 6/1, the intensity of the N 1s peak is small, indicating a small content of N in these films. We also note that the FWHM of the N 1s peak is large which might indicate that N exists in more than one environmental configuration. It is well known that in XPS, non-equivalent atoms of the same element in a solid give rise to core level peaks with measurably

different BEs termed ‘chemical shift’. In order to estimate the chemical composition of the films and identify the chemical environment around the N atoms in these films, we curve fitted the N 1s core level spectra for the two films containing N. Figure 3 shows a two peak fit of the N 1s spectrum of the 6/1 film. The BE of the higher intensity peak is at 397.0 eV labelled N 1s, while that of the lower intensity peak is at 399.2 eV, labelled N 1s_x. The literature shows that the BE of the N 1s core level peak is very sensitive to the chemical environment of the N atom. It varies from 396 eV to 408 eV (Moulder et al., 1992). We follow the assignment of the low BE peak as was done by Shinn and Tsang, 1991, that is the peak at 397 eV, labelled N 1s, to atomic nitrogen (β-N) and that at 399.2 eV, labelled N 1s_x, is due to formation of oxynitride (ZnO_{1-x}N_x). The N atoms could have been substituted for O atoms of ZnO to form ZnO_{1-x}N_x (Tabet et al., 2007a).

Figure 2 N 1s core level spectra for the four films analysed (see online version for colour)

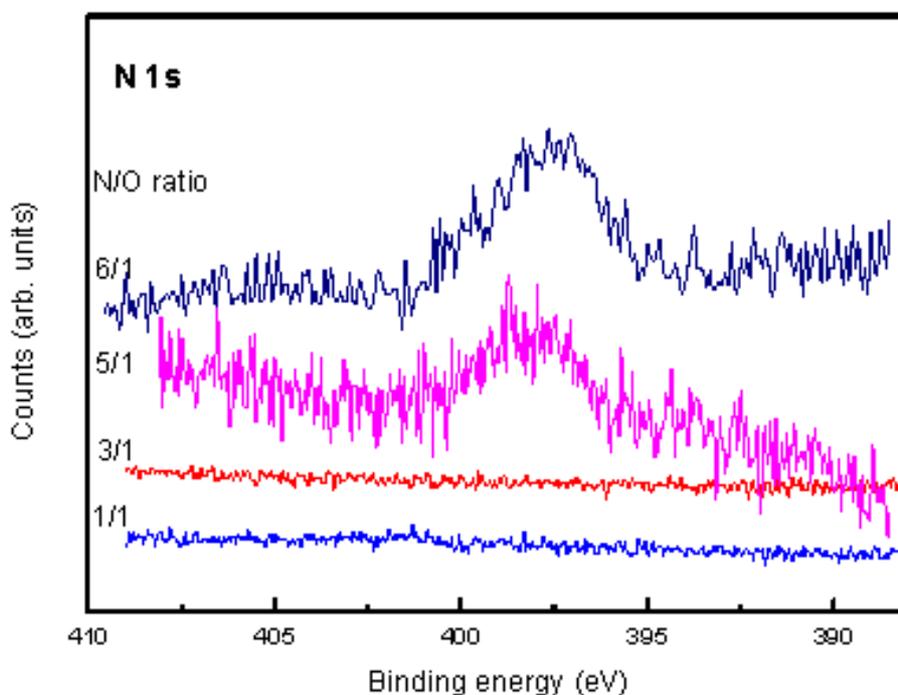
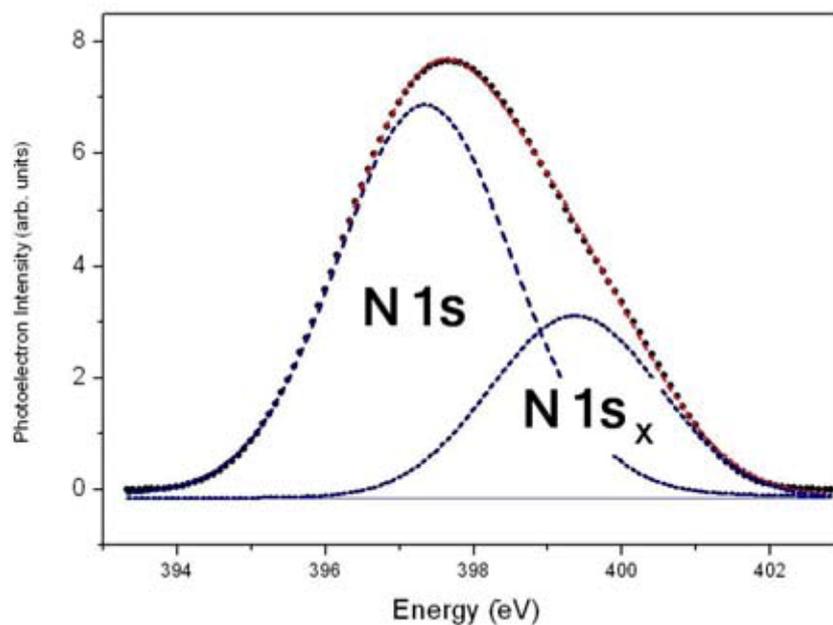


Figure 4 shows the O 1s core level spectra of the as grown N-doped ZnO films. We notice in the four spectra a main peak at a BE of 531.5 eV and a shoulder at a BE of 533.5 eV. The main peak is assigned to oxygen atoms in Zn-O-Zn configuration, while the shoulder has been assigned by many authors to the presence of water moisture, since the BE of H₂O is at 533 eV (Moulder et al., 1992; Tabet et al., 2007a; Meng et al., 1994). An example of the fitting of the O 1s to two contributions is shown in Figure 5 for the N/O ratio of 5/1.

Figure 3 Curve fitted N 1s spectrum for the N/O ratio of 6/1 (see online version for colours)

Note: The spectrum is fitted with two contributions.

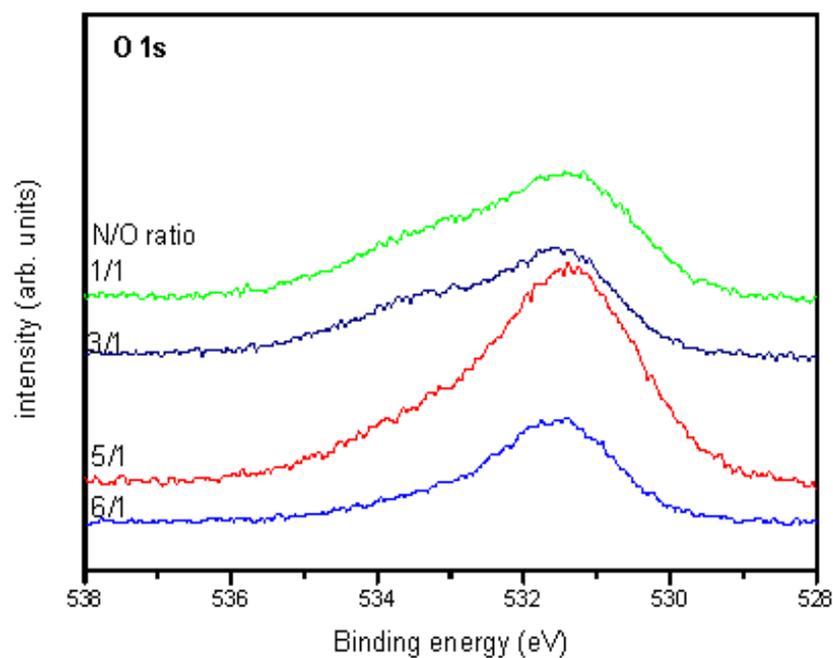
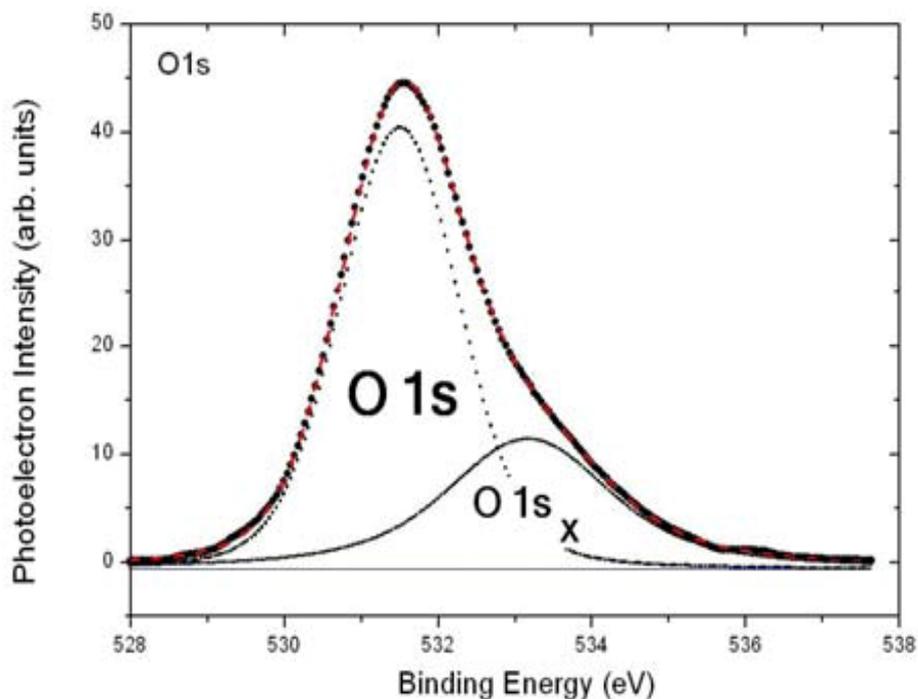
Figure 4 O 1s core level spectra for the four films analysed (see online version for colours)

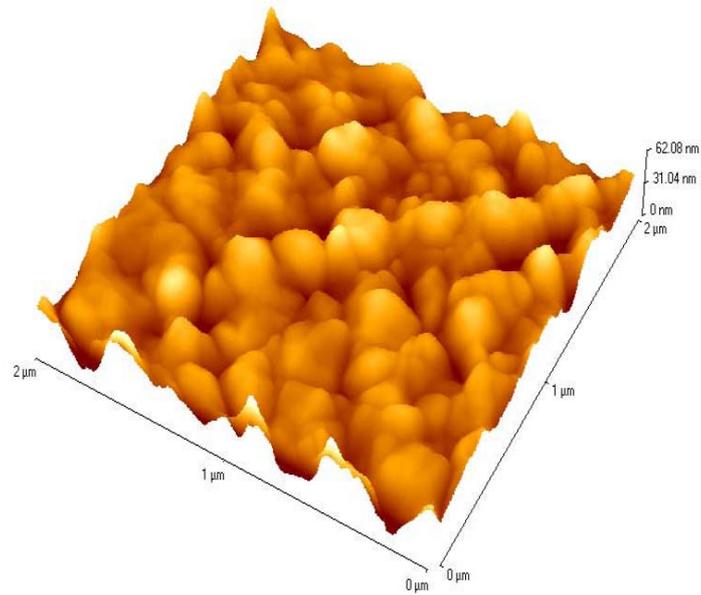
Figure 5 Curve fitted O 1s spectrum for the N/O ratio of 5/1 (see online version for colours)

Note: The spectrum is fitted with two contributions.

It should be pointed out that the Zn2p peak was a single peak in all XPS spectra because of the small chemical shift (< 0.2 eV for the oxide compared to the metallic zinc) and therefore cannot be resolved since the energy resolution of our XPS instrument is ~ 1.0 eV. We estimated the content of N in the 5/1 and 6/1 films as $\sim 1.5\%$ and 4.5% , respectively.

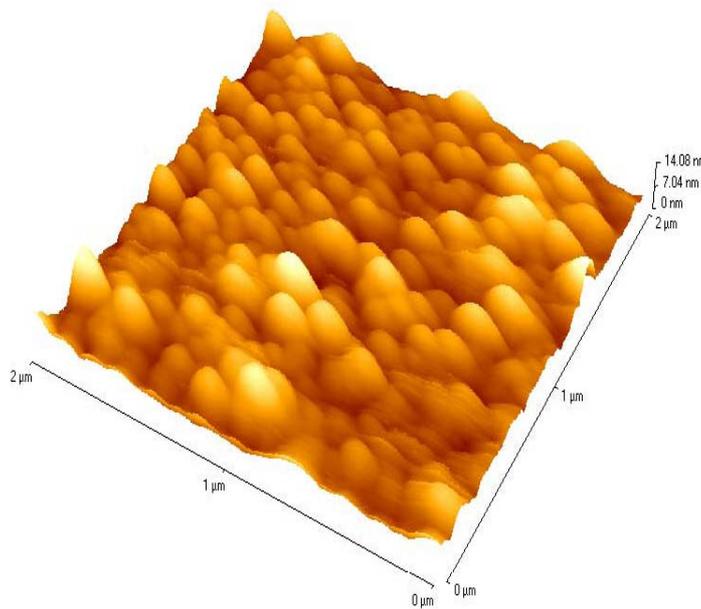
AFM observations were carried out using the tapping mode to study the morphology of the films. Figures 6 and 7 show the AFM image of 1/1 film and 6/1, respectively taken over an area of $2 \times 2 \mu\text{m}^2$ of the film. We can see from Figure 6 that the grains have different sizes and most importantly are randomly oriented which is in agreement with the absence of texture of the films as indicated by XRD pattern. A direct estimation of the average diameter of the small size grains is ~ 60 nm, while that of the large grains is ~ 160 nm. The AFM image of the 6/1 film shows grains of different sizes but all oriented in the same direction which confirms the XRD findings. An estimate of the small grain size diameter is ~ 60 nm, while that of the large grain size is ~ 140 nm. This result shows that Scherrer's formula underestimate the grain size of the films. It seems from these findings that N is responsible for the strong texture.

Figure 6 AFM image of N doped ZnO film with N/O content 1/1 (see online version for colours)



Note: We see the randomness of the grains orientation in the film.

Figure 7 AFM image of N doped ZnO film with N/O content 6/1 (see online version for colours)



Note: We see the texture of the film.

4 Conclusions

We have successfully synthesised N-doped ZnO thin films by DC magnetron reactive plasma. The structure and properties of the films were analysed by XRD, XPS and AFM techniques. The results show that N is introduced in small quantities in films grown at N/O mixing ratio of 5/1 and higher. We also showed that for the films containing nitrogen are strongly textured along (002) direction. The XPS shows that nitrogen is present in different forms including atomic N and N bonded to the ZnO probably forming oxynitride structure. The AFM images confirmed the texture of the 5/1 and 6/1 films and revealed the presence of grains of various shapes and sizes in the non-textured samples.

Acknowledgements

This work was supported by King Fahd University of Petroleum and Minerals under Project INT 299/2006.

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