

# Orbital hybridization, crystal structure and anomalous resistivity of ultrathin CrZr<sub>x</sub> alloy films on polymeric substrates

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The orbital hybridization and crystal structure are experimentally explored for ultrathin chrome zirconium (CrZr<sub>x</sub>) alloy films co-sputtered on precoated polymeric substrates. We determine the level of orbital hybridization and crystal structure using X-ray photoelectron spectroscopy and electron diffraction. Body-centred cubic and  $\Omega$ -hexagonally close-packed phases are observed to coexist in the sputtered Cr-based films. Experiments reveal the orbital hybridization and crystal structure combine to produce anomalous resistivity for these ultrathin films.

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Ultrathin films (thickness of tens of nanometres) on polymeric substrates provide design freedom for the creation of advanced devices, while concurrently presenting challenges for their manufacture, namely temperature limitations during deposition of the desired ultrathin films. An example of a common application for such ultrathin film coatings is in electrical devices, when metals [1], metal alloys [2], metal oxides [3] or conductive polymers [4] are employed within the multilayer system. Of considerable interest are the various alloys employing transition metals, which lead to materials of interest such as quasicrystals [5,6]. The use of transition metal alloys in ultrathin film coatings is becoming more prevalent [7–9], with their application to polymeric substrates presenting an emerging direction in materials science [10].

Some of the more recent studies have focused on the change in magnetic [11] and electrical [12] properties for a variety of alloys, which underpins such modern technologies as non-volatile data storage. Of particular interest in such studies are the binary transition metal alloys, which are simple systems that display much of the exotic behaviour of much more complex materials

[11]. Such transition metal alloys can be investigated with respect to the resistivity–structure relationship, as they also undergo certain phase transformations, for example from the body-centred cubic (bcc) phase to the  $\Omega$ -hexagonally close-packed ( $\Omega$ -hcp) phase through rapid quenching from high temperature [13] or the application of high pressure [14]. However, these transformation methods are not appropriate within the context of this study as neither these is amenable to the use of polymeric substrates. In contrast, magnetron co-sputtering, sometimes referred to as a diffusionless vapour quenching process, lends itself to the use of such substrates and is commonly employed to deposit ultrathin film coatings of transition metal alloys. Herein, the elements of Cr and Zr were co-sputtered from respective targets in an Ar environment onto rotating precoated polymeric substrates. These substrates were heated to 85 °C and the base pressure of the reactor was  $1 \times 10^{-4}$  mbar, as per previous studies [15]. Unlike the majority of previous literature on this topic, the alloy herein consists predominantly of a bcc transition metal, Cr. The previous observations of the  $\Omega$ -hcp phase have been with alloys whose predominant element has been hcp, such as Zr–Fe, Zr–Co, Zr–Ni and Zr–Cu [16].

Each composition of the CrZr<sub>x</sub> alloy (quantified by the parameter  $x$ ) was generated by changing the Zr

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deposition rate relative to the Cr, with the deposition time adjusted to achieve an average film thickness across all samples of  $60 \pm 2.7$  nm as determined by atomic force microscope imaging (NT-MDT).

Here we study these ultrathin  $\text{CrZr}_x$  alloy films using X-ray photoelectron spectroscopy (XPS; Specs) and electron diffraction (Philips CM200 TEM; sample preparation as per Ref. [10]) to determine the change in electron and crystal structure. These results are then correlated with the electrical properties of the ultrathin films through measurement of the resistivity as a function of temperature. Studies of this nature for binary transition metals have not been reported in the literature. The resistivity was calculated from the sheet resistance measurements made using a 4-point probe (RM3, Jandel Engineering), taken as a function of temperature (Peltier system) with a relative humidity of  $35 \pm 5\%$ .

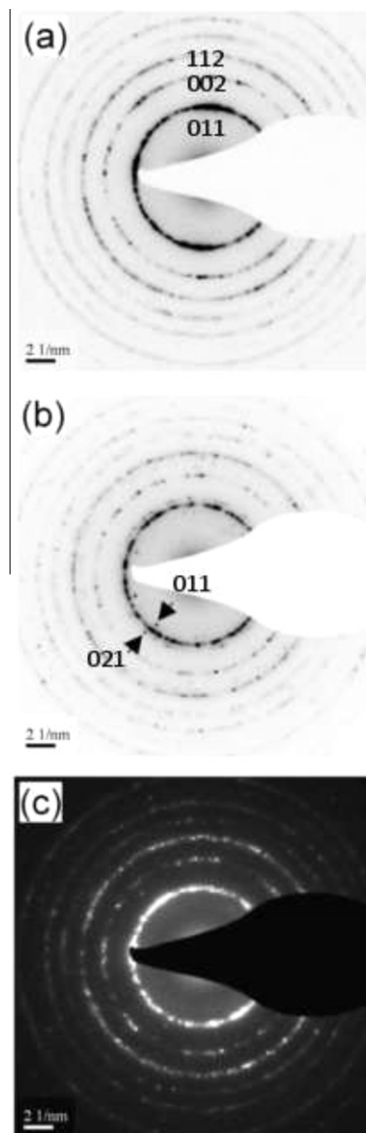
For each of the ultrathin  $\text{CrZr}_x$  alloy films, the electron diffraction pattern was collected and analysed with respect to the major constituents within the coating, as shown in Figure 1.

Two transition concentrations are defined in the electron diffraction analysis where phase transformations are observed. These transitions are at  $x = 0.05$  (bcc to bcc plus  $\Omega$ -hcp) and  $x = 0.15$  (bcc plus  $\Omega$ -hcp to bcc plus amorphous). The  $\Omega$ -hcp phase therefore exists in the range of  $x \in (0.05, 0.15)$  for the  $\text{CrZr}_x$  alloy studied herein. Its coexistence with other phases has been experimentally observed for magnetron-sputtered thick films (ca.  $4.2 \mu\text{m}$ ) of Zr on Cr-rich steels [17] and studies of other transition metal alloys employing thicker films or bulk material [18].

Concurrent with the structural changes for increasing Zr concentration in the alloy, the binding energies from XPS for both Cr  $2p$  and Zr  $3p$  shift to higher energy (Fig. 2). The positive shifts for both elements in the alloy are expected, as electron screening leads to minimal charge transfer between transition metals in an alloy [19]. The relative change in binding energy coincides with changes in the crystal structure. In particular, the slope of the binding energy vs.  $x$  for the Zr  $3p$  state changes when the amorphous phase is observed (see Fig. 2b). For metals this can be rationalized, given that the core level binding energies are sensitive to the atomic neighbourhood (neighbouring atom type, coordination number and interatomic distances) [19].

Within the respective states, there is a change in hybridization quantified by the relative binding energies of the  $p_{1/2}$  and  $p_{3/2}$  states (Cr  $2p$  and Zr  $3p$ , Fig. 3). Upon observation of the  $\Omega$ -hcp phase, there is a measurable change in the Zr  $3p$  hybridization (a change in binding energy from 12 to 13.5 eV). While the Cr  $2p$  shows some variation in the  $\Omega$ -hcp phase region, it is minimal compared to the Zr  $3p$ . As transition metals are known for their valence  $d$ -orbital hybridization with the  $s$ - $p$  orbitals of neighbouring ligands, it is plausible to assume that the Cr  $3d$  orbitals are undergoing hybridization with the Zr  $3p$  orbitals.

The crystal structure and electron orbital interaction manifest in the electrical resistivity of the ultrathin film. The electrical resistivity ( $\rho$ , ohm cm) of the ultrathin



**Figure 1.** Electron diffraction patterns illustrating the different phase compositions observed in the co-sputtered ultrathin  $\text{CrZr}_x$  films. (a) At concentrations below  $x = 0.05$  a bcc phase is observed with provided miller indices. (b) At concentrations of  $x \in (0.05, 0.15)$  a bcc and  $\Omega$ -hcp phase (arrows) are observed to coexist, with the Miller indices of the  $\Omega$ -hcp phase provided. Both (a) and (b) have been inverted to give clarity of the structure. (c) At concentrations greater than  $x = 0.15$  a bcc and amorphous phase are observed to coexist; the image is not inverted to illustrate the amorphous background haze.

$\text{CrZr}_x$  alloy films was determined from the measured sheet resistance ( $R_s$ , ohm square $^{-1}$ ) and film thickness ( $t$ , cm) using  $\rho = (R_s \cdot t)$ . The temperature range was limited from room temperature to  $50^\circ\text{C}$  to guarantee the polymeric substrate remained unchanged. These results are the first report of the resistivity–temperature relationship for ultrathin films of transition metal alloys, particularly those deposited onto polymeric substrates without any post-deposition treatment.

From these results presented in Fig. 4, an anomalous resistivity–temperature relationship is observed in the concentration range of  $x \in (0.05, 0.15)$ , where the  $\Omega$ -hcp phase coexists with the bcc phase. As the temperature increases there is little response in the resistivity,

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