

# Characterization of ZrO<sub>2</sub> and SiC ceramic thin films prepared by electrostatic atomization

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ZrO<sub>2</sub> and SiC ceramic thin films and their bilayer have been successfully prepared by a newly developed electrostatic atomization technique. This technique can generate fine spray of ceramic suspensions in a micrometer sized range with a narrow size distribution which is crucial for preparation of uniform thin films of these ceramic materials. Compared to some other thin film deposition techniques, such as Chemical vapour deposition (CVD), physical vapour deposition (PVD) and plasma spray (PS) etc. the thin film deposition process using electrostatic atomization is not only cheap but also controllable. The prepared ZrO<sub>2</sub> and SiC thin films were investigated using scanning electron microscopy (SEM) and energy dispersion analysis (EDA) techniques. These thin films were observed to be homogenous with a particle size less than 10 μm. The ZrO<sub>2</sub>-SiC bilayer was found to have an abrupt interface, implying that the deposition process is controllable and also that functionally graded ceramic/ceramic materials can be prepared in this way if the thickness of each layer is accurately controlled. © 2001 Kluwer Academic Publishers

## 1. Introduction

Over the past two decades, there has been a significant growth of interest in research and development in the advanced ceramic industry. The advanced ceramic industry covers a wide and diverse range of products of which ceramic thin films and coatings are one of the most important applications, especially in electrical, electronic electro-mechanical and thermal industries etc., in order to solve many corrosion, electrical insulation, wear and thermal protection problems. The special physical properties of ceramics derive from their fundamental bonds which are primarily of a mixed ionic/covalent type rather than a metallic type. This results in, for most ceramics, a completely filled electronic valence bands separated by a wide forbidden band from completely empty electronic conduction bands. As a result, most ceramic materials are electrical insulators. However, if some additives are introduced into their structure, the electronic and optical properties of the ceramics can be tailored to make them semiconductors and electro-optic materials which are widely used for wave guides, modulators, detectors and so on. For most applications, ceramic materials are in the form of thin films and coatings.

The quality of ceramic thin films and coatings is heavily dependent on the size and size distribution of the ceramic powder particles during deposition process [1]. This is because fine particles with a narrow size distribution have the effect of limiting the size of voids between particles, this enables these ceramic thin films and coatings to be deposited with high homogeneity and without flaws. This, in turn, determines the mechani-

cal and electrical properties of the ceramic materials. Furthermore, a smaller particle size will lead to a lower sintering temperature. This is certainly favourable for industrial applications. Basically, the challenge of producing high quality ceramic thin films and coatings is to generate fine powder particles in a micrometer sized range, with a narrow size distribution, in a controllable way during deposition.

In searching for a new micro-fabrication technology for ceramic thin films and coatings, electrostatic atomization in cone-jet mode exhibits a very promising potential with its inherent capability of producing fine droplets in micro and sub-micrometer range with a narrow size distribution [2–5]. The reason for monodispersity of electrospray in cone jet mode is that axisymmetric surface wave instabilities predominate the liquid jet break-up process, which results in a constant ratio between primary droplet diameter and liquid jet diameter. This turns into a question whether or not fine droplets of ceramic suspensions can be generated in the same way.

Compared with other thin film deposition technologies like chemical vapour deposition (CVD), physical vapour deposition (PVD) and plasma spraying (PS), electrostatic atomization is a relatively inexpensive process and also has the added advantage of having the potential to control and deposit multi-layer coatings. van Zomern and co-workers [6] demonstrated the possibility of using electrospray technique to synthesize LiMn<sub>2</sub>O<sub>4</sub> thin film, but the particle size was found not to be uniform, probably due to technical problem with their experimental set-up. Chen *et al.* [7] prepared uniform TiO<sub>2</sub> thin films and ZrO<sub>2</sub> fine powders

using electrospray deposition. However, in both studies, the thin films and fine powders were synthesized by chemical reaction of precursor solutions and additives. This may leave some chemical residuals or impurities in the thin films, which may not be suitable for some cases where high purity thin films are needed. Recently, Teng and co-workers [8] have demonstrated the feasibility of electrostatically atomizing a suspension containing a ceramic filler to produce fine droplets. The ceramic powder particles deposited on the substrate were between 2 and 15  $\mu\text{m}$  which is still considered not to be narrow enough in size distribution. The droplet size in their work was roughly estimated from the relics of the particles on the substrate. The real size and size distribution of the spray during transportation to the substrate was not measured. In our previous work [9], it was shown that fine particles in the range of a few micrometers, even sub-micrometers, with a very narrow size distribution can be deposited on substrates using electrospray. However, comprehensive investigation on deposited thin films was not conducted.

In this paper, low coverage, high coverage and bilayers of  $\text{ZrO}_2$  and SiC ceramic materials were deposited using electrostatic atomization in cone-jet mode. The morphologies and microstructures of the thin films were investigated by scanning electron microscope (SEM). The compositions of the thin films were analysed using energy dispersion analysis technique (EDA). A high shutter speed CCD camera with a fast image grabbing system was employed for monitoring the electrospray mode throughout the experiments.

## 2. Experimental details

The experimental configuration is schematically shown in Fig. 1. The electrospray system is composed of a stainless steel capillary with an inner diameter of 0.23 mm and an outer diameter of 0.51 mm. A high voltage (4–6 kV) was applied to the capillary. A concentric ring electrode with an inner diameter of 15 mm

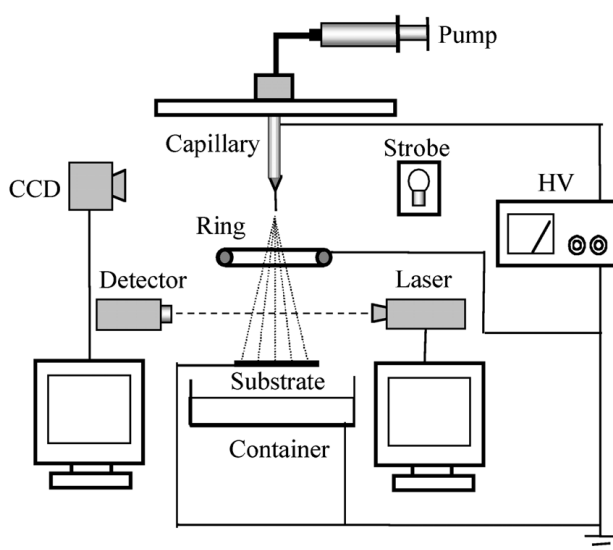


Figure 1 The schematic diagram of the experimental set-up.

was arranged 8 mm away from the capillary tip. This electrode was connected to ground potential. A metallic container which also served as an electrode was grounded. Ceramic suspensions were fed to the capillary at a flow rate from 0.5 to 1.5 ml/hr, using a Harvard 11 syringe pump (Harvard Apparatus, USA). The suspension spray processes were monitored using a high shutter speed TM-765 CCD camera (Pulnix Europe, UK) together with fast image grabbing software (Image 1.42) installed in a Macintosh computer. The size and size distribution of suspensions were measured using laser diffraction technique (System-Partikel-Technik, Germany). Silicon and Cr-Fe alloy substrates were grounded and positioned 10 mm below the ring to collect droplets during deposition. The morphologies, microstructures and compositions of the thin films on the substrates were examined by SEM and EDA (Hitachi, Japan) after deposition.

Formulation of the ceramic suspension is the first and key stage for electrospray deposition, since the properties of the suspension play an important role in electrostatic atomization. For example, conductivity of the suspension must fall in a suitable range in order to obtain a stable cone-jet [10]. In this work, fine zirconia powder HYY-3 with an average particle size of 0.47  $\mu\text{m}$  (Mandoval Limited, UK) and fine SiC powder with an average particle size of 1.0  $\mu\text{m}$  (PI-KEM, UK) were used. Liquids in ceramic suspension function as a medium to suspend and disperse the ceramic particles. In the present work, the  $\text{ZrO}_2$  suspension was prepared by dispersing 5%  $\text{ZrO}_2$  powder in weight in a solution of distilled water and ethanol (Aldrich) mixture of a ratio of 1 : 1 by volume. The SiC suspension was formulated by dispersing 1.3% SiC powder in weight in pure ethanol (Aldrich). These suspensions were subjected to ultrasonic agitation and electrical stirring with a magnetic bar for 30 minutes each. It was found that the suspensions were stable without serious sedimentation for several days, which is long enough for completion of experiments.

## 3. Results and discussions

In order to deposit uniform, dense thin films, fine droplets of ceramic suspensions must be generated first. Under the influence of different flow rate and applied potential, aerosol can be generated in various different modes such as dripping mode, fully-developed mode, cone-jet mode, multi-jet mode etc. Among these modes, electrostatic atomization in cone-jet mode is the most suitable technique to meet this requirement due to its inherent capability of producing monodispersed fine droplets in a controllable way. Details of this were published in our previous work [11].

Fig. 2 shows a close examination of a typical cone-jet generated at the flow rate of 0.8 ml/hr and the potential of 4.5 kV, using  $\text{ZrO}_2$  suspension. From the CCD image, the diameter of the jet close to the tip of the cone was estimated to be around 4  $\mu\text{m}$ . The length of the jet was measured to be about 200  $\mu\text{m}$ .

From Rayleigh charge limit [12], one can easily deduce Rayleigh charge limit in the form of charge to

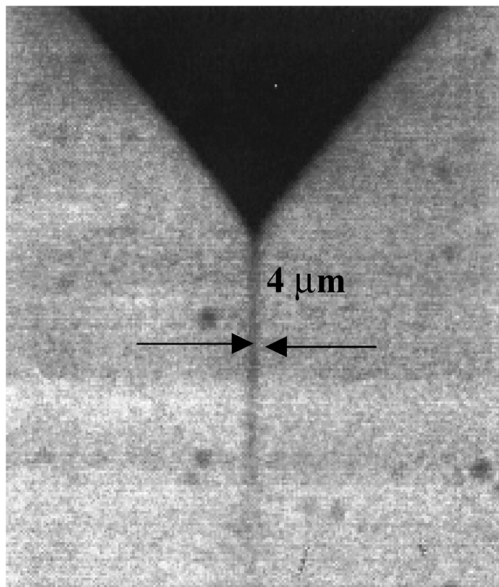


Figure 2 CCD image shows a close examination of cone-jet.

mass ratio as below:

$$\frac{q_R}{m} = 6 \left( \frac{\epsilon_0 \gamma}{\rho^2 r^3} \right)^{\frac{1}{2}}$$

Where  $r$  is the radius of the droplets,  $\rho$  is density of the suspension,  $\gamma$  is surface tension,  $\epsilon_0$  is dielectric constant of vacuum. Experimentally, charge to mass ratio can be obtained by measuring spray current, liquid flow rate and liquid density, which is given below:

$$\frac{q}{m} = \frac{I}{Q\rho}$$

From our droplet size and spray current measurements, Rayleigh charge to mass ratio can be calculated to be about 1.09 C/kg and 1.10 C/kg for  $ZrO_2$  and SiC suspensions respectively. The actual charge to mass ratio of sprayed  $ZrO_2$  and SiC suspensions can be worked out to be about 0.61 C/kg and 0.31 C/kg respectively, which are all smaller than corresponding Rayleigh charge to mass ratios. This suggests that the spraying of the suspensions should obey Rayleigh break-up process. According to conventional Rayleigh theory, the ratio of droplet diameter to the jet diameter ( $\phi_D/\phi_J$ ) is about 1.89 for liquid jets of low viscosity without an electric charge. For charged jets, theoretical study by Neukermans [13], Bailey and Balachandran [14] and experimental study by Cloupeau *et al.* [5] show that the ratio of ( $\phi_D/\phi_J$ ) does not change significantly provided the surface charge density is below Rayleigh limit. This condition is obviously applicable to our case. This indicates that the droplet size immediately after break-up of the jet should be in the range of a few micrometers (7–8  $\mu m$ ) due to a 4  $\mu m$  jet. It should be noted here that the size of droplets further down in the aerosol plume is smaller due to evaporation of the organic solvent (ethanol) in the ceramic suspensions during transportation. A typical droplet size distribution measured below the ring electrode is shown in Fig. 3. The mean size of

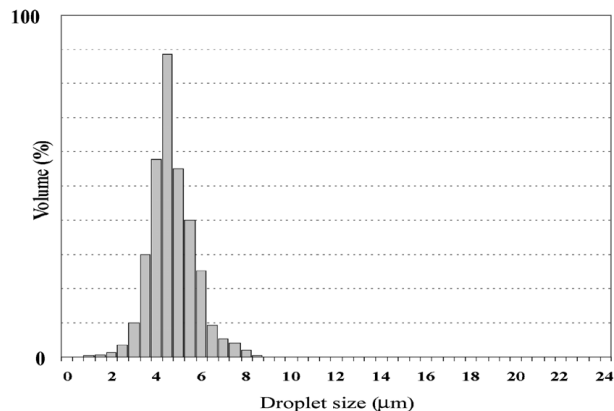


Figure 3 A typical size distribution curve.

the droplet is about 4–5  $\mu m$ . This indeed indicates that fine droplets of ceramic suspensions can be generated in this way.

Fig. 4 shows SEM characterisation of low coverage  $ZrO_2$  thin films deposited on silicon substrates. From Fig. 4a–c, it can be seen that the ceramic particles are reasonably evenly distributed on the surfaces. This is because during the spray process, the droplets are charged, which prevents droplets or particles from agglomeration due to electrostatic repulsive force. The particle size is estimated to be in the range of about 0.1–1.0  $\mu m$  which, in fact, is the original size of the ceramic powder particles. If the ceramic powder was ball-milled before suspension formulation, the particle size should be even uniform. This means that the fine ceramic particles can be deposited on substrate individually. Therefore, this technique can be also employed to prepare ultra fine powder if the experimental set-up is arranged in such a way which allows solvents in the suspensions to completely evaporate before the powder particles land on the substrates. The ceramic particles in Fig. 4a–c were deposited at the same flow rate of 0.6 ml/hr for the same duration of 2 minutes, but at different applied voltages of 6.0, 5.6 and 5.0 kV respectively. From Fig. 4a–c, one can find that the distribution density of those particles on the surfaces is different. A higher applied voltage, leading to a smaller droplet size, results in a less dense deposited layer. The reason for this is probably that when the droplet size is smaller, these droplets are likely to have a higher charge-to-mass ratio [2], hence larger space charge effect. Furthermore smaller droplets have lower inertia. All these factors are favourable for smaller droplets to spray at a larger spray angle after breakup of the jet. This clearly demonstrates that the dispersion and deposition patterns on substrates can be controlled by controlling the applied potential to the capillary.

Fig. 5 shows a SEM image of a high coverage  $ZrO_2$  thin film deposited at a flow rate of 0.8 ml/hr and a potential of around 4 kV. It can be clearly seen that the deposited thin film is very homogeneous. The average particle size is less than 10  $\mu m$ . These particles are closely packed together to form a uniform and dense thin film. A high magnification SEM investigation on one particle (shown in Fig. 6) indicates that these particles are agglomerates. They contain many

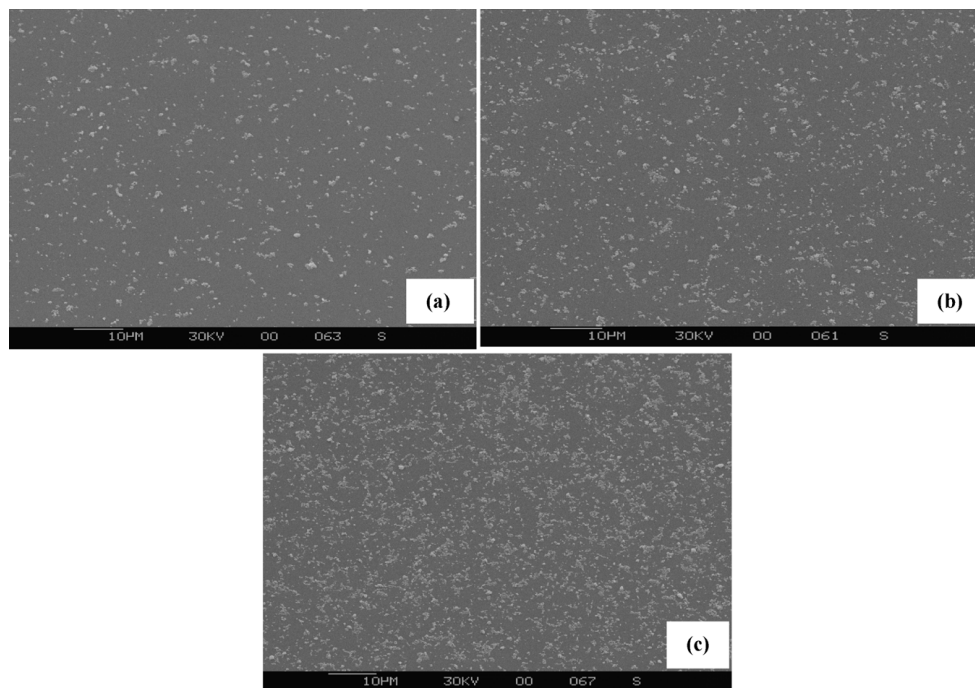


Figure 4 SEM images show the influence of applied potential on distribution density of ceramic particles deposited on substrate.

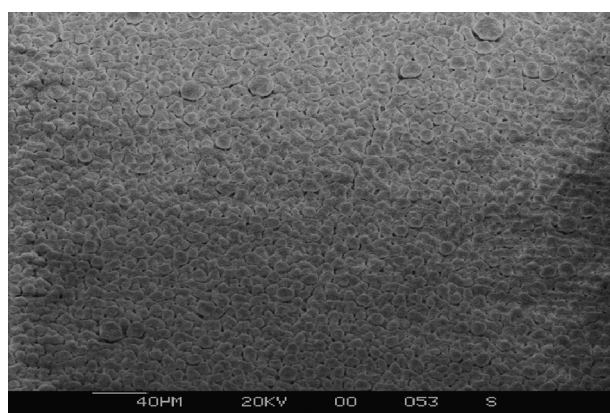


Figure 5 SEM image shows a very homogeneous morphology of ZrO<sub>2</sub> thin film.

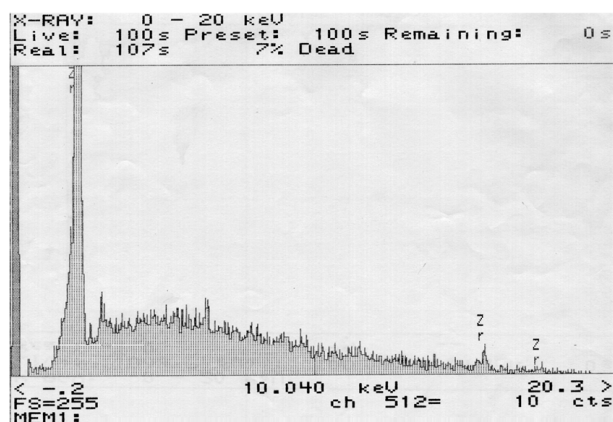


Figure 7 EDA spectrum of ZrO<sub>2</sub> thin film shows a strong and two weak Zr peaks.

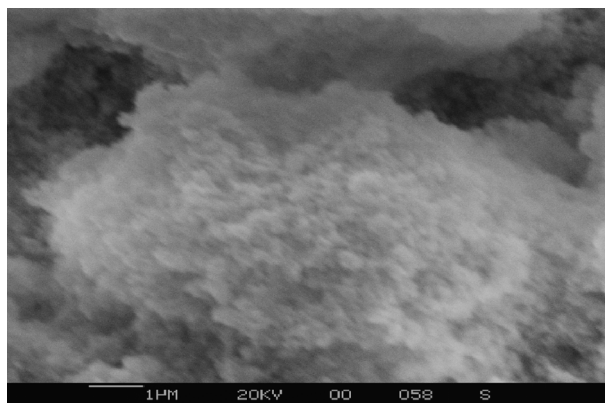


Figure 6 A high magnification SEM image of one Zr<sub>2</sub> agglomerate.

much smaller particles with an average size of half a micrometer which is actually the original size of the dry powder particles. It is understandable that there is a high tendency for agglomeration of ZrO<sub>2</sub> powder particles because of its comparatively high surface area

per unit weight ( $7 \text{ m}^2/\text{g}$ ), which possess comparatively high surface energy. Agglomeration can lower the total surface energy to stabilize the system. EDA (Energy Dispersion Analysis) study of the thin film (see Fig. 7) shows strong Zr peaks in the spectrum, indicating that the observed micro-features really result from the ZrO<sub>2</sub> thin film instead of solvent residuals and contaminants.

Fig. 8 is a SEM image of SiC thin film deposited at a flow rate of 1.5 ml/hr and a potential of 5 kV. This image also shows a homogeneous morphology, but compared to ZrO<sub>2</sub>, SiC thin film is more porous. Agglomeration seems to occur again in the film, giving an average agglomerate size of  $5 \mu\text{m}$ . Since the surface area per unit weight ( $0.2 \text{ m}^2/\text{g}$ ) of SiC is much lower than that of ZrO<sub>2</sub>. The agglomeration tendency is therefore much weaker, hence smaller agglomerate size. A close examination on the microstructure of agglomerates shown in Fig. 9 shows that flake-shaped SiC particles with an average size of  $1 \mu\text{m}$  are loosely packed together. This also supports the weak agglomeration of SiC. The

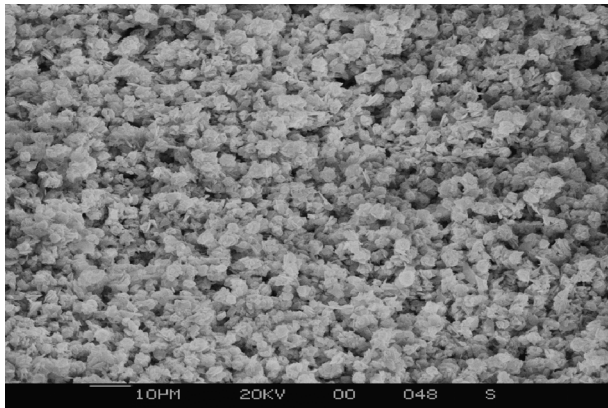


Figure 8 SEM image shows a very homogenous morphology of SiC thin film.

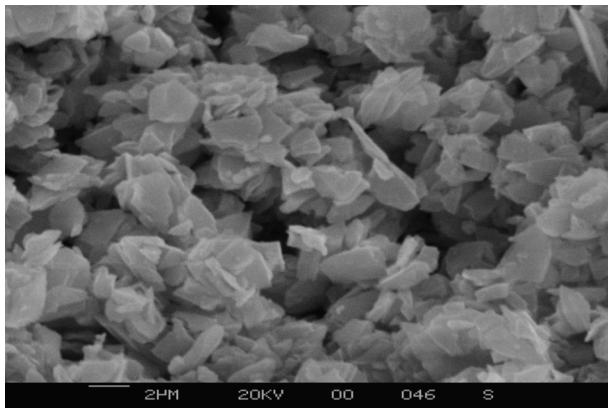


Figure 9 A high magnification SEM image shows individual SiC particles.

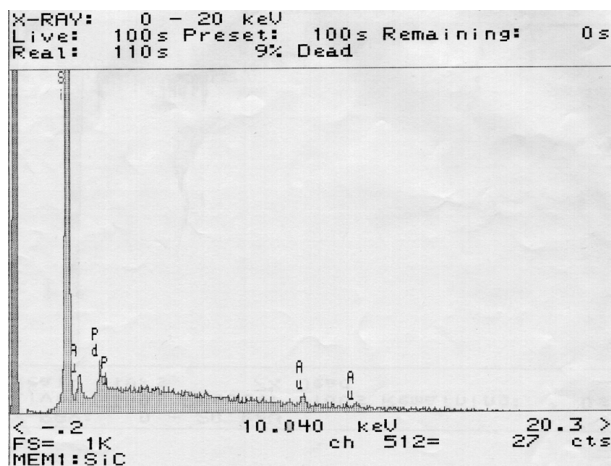


Figure 10 EDA spectrum of SiC thin film shows a strong Si peak.

special shape of SiC particles may also prevent them being packed as closely as ZrO<sub>2</sub>. EDA analysis of the thin film (Fig. 10) showing a strong Si peak in the spectrum verifies SiC composition in the film. The Au and Pd peaks result from the Au-Pd thin coating deposited on top of the SiC thin film for SEM investigation. These peaks are not labelled in other EDA spectra. Small and uniform particle size in “green form” of these thin films prepared by electrostatic atomization has the effects of reducing sintering temperature and crack possibil-

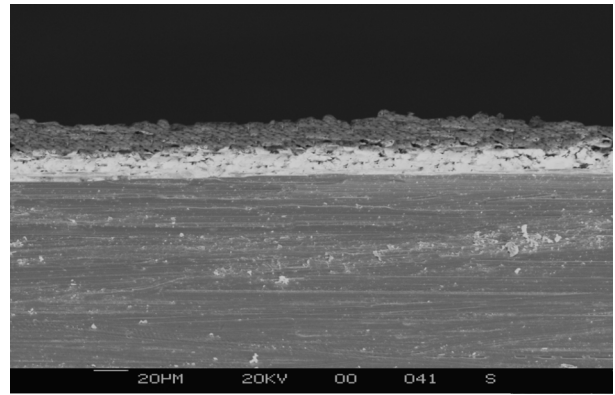


Figure 11 SEM image shows the cross-section of SiC-ZrO<sub>2</sub> bilayer.

ity during sintering process, which is certainly highly demanded by many industries.

Attempts of depositing SiC-ZrO<sub>2</sub> bilayers have been also made. Fig. 11 shows a close examination of the cross-section of the bilayer. A very smooth top surface can be clearly seen from the image. The total thickness of the bilayer is about 40 μm with an abrupt interface between the two layers, indicating that the deposition process can be well-controlled. More complex and functionally graded ceramic/ceramic structures should be able to be prepared using this technique if composition and thickness are properly controlled.

#### 4. Conclusions

ZrO<sub>2</sub> and SiC ceramic thin films and their bilayer have been prepared using electrostatic atomization in cone-jet mode. SEM examinations of the microstructures of these thin films show that the films are very homogenous with a uniform particle size less than 10 μm. The deposition of a very thin bilayer with an abrupt interface indicates that electrostatic spray process can be well controlled. EDA analysis of these thin films confirms that the micro-features really result from these ceramic materials instead of contamination or solvents. Electrostatic atomization technique can be also utilized for preparation of ultra fine powder due to its characteristic of charged spray.

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