JOURNAL OF MATERIALS SCIENCE **38** (2003) 3239–3244

# Morphological instability of $ZrO_2$ crystallites formed by CVD technique operated under atmospheric pressure

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Zirconium oxide ($ZrO_2$) crystallites were deposited using a chemical-vapor-deposition apparatus operated under atmospheric pressure on a silicon substrate. The X-ray diffraction pattern reveals that the crystallites have a preferred crystallographic orientation along the $ZrO_2$ $\langle 200 \rangle$ direction and ascertains the presence of the monoclinic structure. The sample morphology indicates the existence of the aggregation of the whisker with a growth rate of 0.5 nm/s, 0.7 nm/s and 0.9 nm/s corresponding to the substrate temperature of 650°C, 680°C and 700°C, respectively. High temperatures introduce morphological instability in the whiskers. The appearance of a dendrite structure is an example of such morphological instability. Furthermore, a noticeable cathodoluminescence emission is observed in the U.V. and blue regions at room temperature.

## 1. Introduction

Engineering ceramics, which are characterized by the ability to bear loads at elevated temperatures, are being extensively considered as promising materials for various structural applications. However, these materials exhibit a low fracture toughness, which affects their reliability and limits their utilization [1].

The most appealing and simple way to improve fracture toughness is to incorporate ceramic whiskers in a composite matrix as toughning and reinforcing agents since the absence of grain boundaries and their very small dimensions that limit the number of imperfections such as dislocation, vacancy cluster, porosity or twins in whiskers have permitted to achieve superior mechanical properties [2, 3]. As a result, the synthesis of mainly non-oxide whiskers has received paramount interests [4–6]. The existence of a large number of investigations on SiC is an illustration of this case. However, at high temperatures, components containing non-oxide whiskers oxidize and their properties degrade [7]. Therefore, it is imperative to synthesize oxide whiskers [8–10].

Zirconium oxide with excellent properties such as, low thermal conductivity and a high thermal expansion coefficient closer to that of metals is widely used as a toughening agent in whisker reinforcement. The synthesis of $ZrO_2$ whiskers, if possible, combined with their superior properties will certainly allow this ceramic material to become one of the best candidates for reinforcing and toughening metal matrix composites (MMC) and ceramic matrix composites (CMC). In order for the whiskers to be used in CMC, their size and morphology, their compatibility with matrix materials and the interfacial bonding between matrix and whiskers are the most important properties that must be considered. The whiskers grown in clumps and bundles make their processing difficult. Therefore, larger diameter whiskers with relatively short aspect ratios and larger diameter ceramic particles will make processing considerably easier [6].

Various techniques can be used in the synthesis of oxide whiskers. For example, m-$ZrO_2$ (monoclinic-zirconia) whiskers were grown hydrothermally from YSZ single crystals by selective dissolution of yttrium in $H_2SO_4$ solution [11]. Wei *et al.* obtained MgO whiskers by the heat treatment of hydrous magnesium oxysulfate (MOS) whiskers at 1000°C [12]. Furthermore, Chang *et al.* reported the growth of single-crystal whiskers on the copper-metallized (Cu/Ti/Si) substrates in an Ar environment, using a conventional sputter deposition technique [13].

Chemical-vapor-deposition (CVD) method operated under atmospheric pressure characterized by low cost and simplicity can be a handy technique for the synthesis of oxide whiskers. The epitaxial polycrystalline films of anatase and the epitaxial whisker of ZnO were the typical examples obtained by this technique [14–19]. The present study was undertaken in an attempt to investigate the growth of highly oriented $ZrO_2$ whiskers under various temperatures by a CVD apparatus operating under atmospheric pressure.

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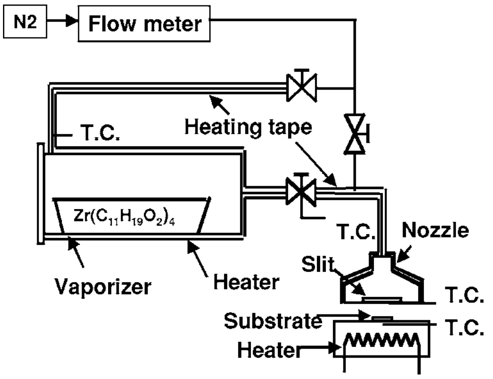

*Figure 1* Schematic diagram of CVD apparatus for $ZrO_2$ whiskers.

## 2. Experimental

The $ZrO_2$ whiskers were synthesized by the CVD technique operated under atmospheric pressure. Fig. 1 shows the schematic diagram of the experimental apparatus. It consists mainly of a vaporizer, a substrate heater and a nozzle. The solid material of the source complex $Zr(C_{11}H_{19}O_2)_4$ (zirconium 2,2,6,6-tetramethyl-3,5-heptadionate, Showa Denko, Co.) was first placed in the vaporizer and vaporized at a temperature of 280°C. The constituents in the vapor phase were transferred through the nozzle by a carrier gas $N_2$ with a flow-rate of 3.2 l/min to form a solid crystallite at the substrate surface. The substrate was heated at 700°C, 680°C and 650°C, respectively, for 2 h. The distance between the nozzle and the substrate was kept constant at 15 mm throughout the experiment. A single crystalline wafer (100) Si was cut into a size of 10 × 10 $\text{mm}^2$, used as the substrate material, and then sequentially ultrasonically cleaned with distilled water, ethanol and acetone.

After the synthesis, the crystal structure was examined using an X-ray diffractometer (MO3XHF, Mac-science, LTD) equipped with a monochromated high intensity Cu $k_\alpha$ radiation (40 kV, 40 mA, $\lambda = 1.54065$ Å) at room temperature. Diffraction pattern of the whiskers was taken with a scan rate of 1°/min over the range $20° < 2\theta < 80°$. The morphology of the whiskers was observed by a field-emission scanning electron microscope (FE-SEM, JSM-6700F, JEOL).

In order to check the wide range of possible applications of the $ZrO_2$ whiskers, cathodoluminescence (CL) of the samples was measured. The CL was taken by electron beam irradiation with an accelerated voltage of 30 kV and an electron current of 50 pA. As an excitation source, a scanning microscope (SEM, JEOL, JSM T300) system equipped with a cathodoluminescence spectrofluorometer was used.

## 3. Results and discussion

The whiskers synthesized by the above technique were analyzed by X-ray diffractometry. The diffraction pattern obtained is shown in Fig. 2. At 700°C, six peaks that appear at 28.8°, 31.6°, 34.3°, 35.5°, 72.7° and 75° are easily identified. They correspond to (−111), (111), (200), (020), (400) and (−313) peaks of the monoclinic zirconium oxide phase. For the whiskers grown at 680°C and at 650°C, the same peaks can be observed, even though their intensity tends to be reduced, especially at 650°C . For all the three temperatures, the monoclinic structure prevails and the whiskers show a strong preferred orientation along the ⟨200⟩ direction.

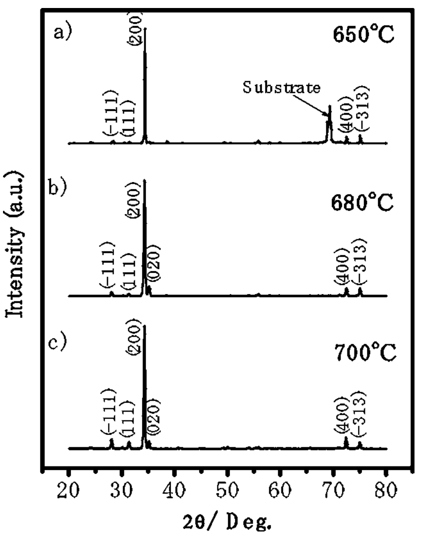

*Figure 2* Diffraction pattern of $ZrO_2$ whiskers at various temperatures.

Fig. 3 shows the SEM micrographs of the $ZrO_2$ whiskers synthesized at various temperatures (650°C, 680°C and 700°C). Regardless of the substrate temperature, homogeneous and oriented $ZrO_2$ whiskers were obtained. At 650°C, the crystallites exhibit a high density and seem to be uniformly distributed. As the deposition temperature increases, the grain size increases and the formation of dendrites begins in a few locations. These dendrites have flower-like shape if observed from the top. The typical morphology of the $ZrO_2$ whiskers synthesized at 700°C is shown in Fig. 4. The normal growth of whiskers, which covers almost the entire surface of the substrate, can be seen in Fig. 4a, while Fig. 4b illustrates the occurrence of the morphological instability leading to the formation of dendrites. Fig. 5 is a perfect illustration of both cases and shows how fast the dendrites grow. This particular aspect will be discussed briefly later.

The dependence of the length and diameter of whiskers on temperature was investigated and the results are shown in Fig. 6. The whisker length and diameter are plotted against the temperature. In Fig. 6, the black circles denote the whisker length while the black squares denote the whisker diameter. From these results, it appears that both the length and diameter of the whiskers increase with increasing the substrate temperature. The whiskers have the following length values: 3.4 $\mu$m, 5 $\mu$m and 7 $\mu$m corresponding to the substrate temperatures of 650°C, 680°C and 700°C, respectively. The diameters of the whiskers are 0.5 $\mu$m, 0.4 $\mu$m and 0.3 $\mu$m for whiskers synthesized at 700°C, 680°C and 650°C, respectively.

Fig. 7 shows the dependence of the growth rate and the population density of the whiskers on the substrate temperature. The whiskers growth rate and the population density of the whiskers are plotted against temperature. The black circles denote the growth rate of

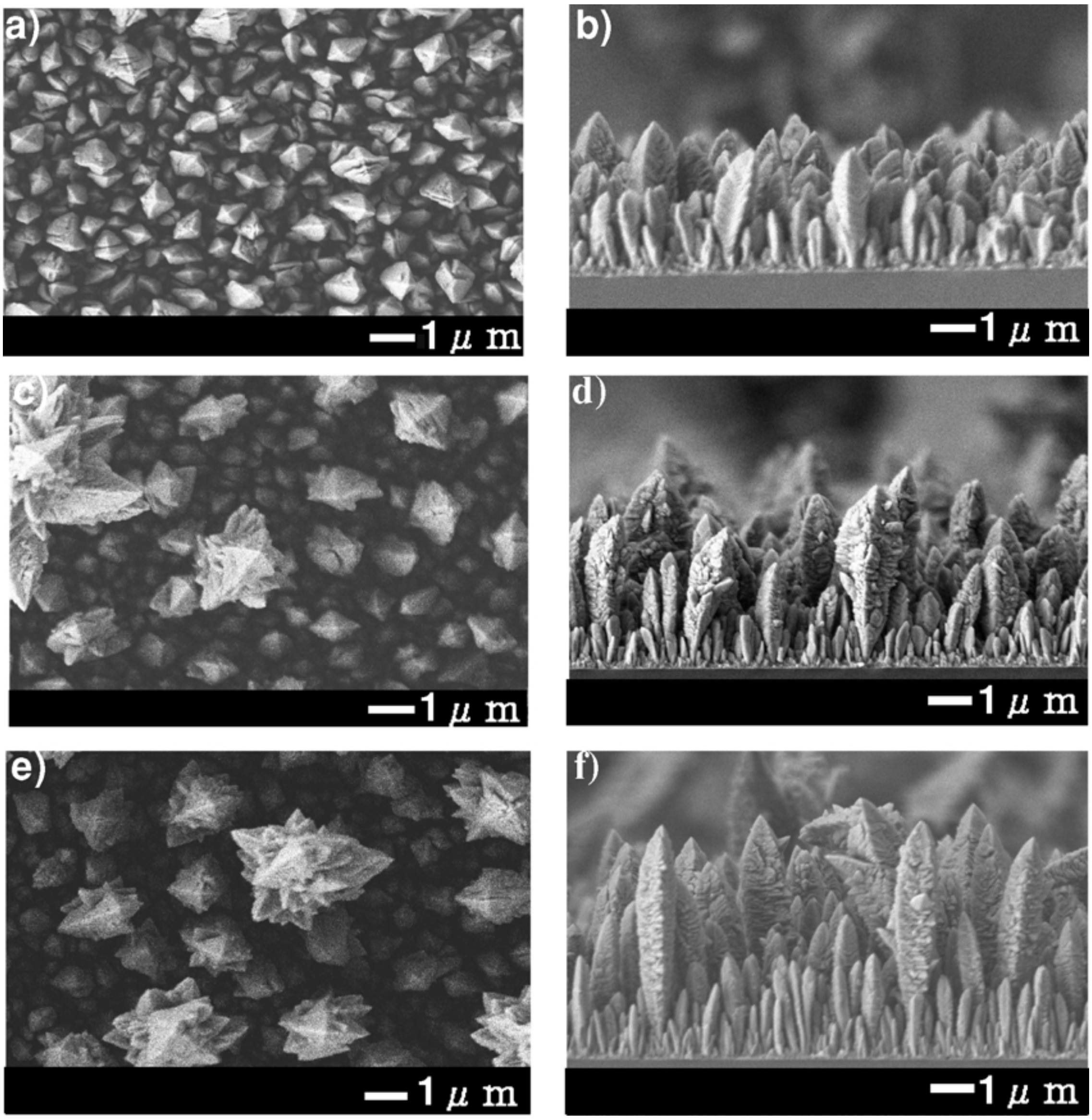

*Figure 3* SEM micrograph of whiskers synthesized at 650°C ((a) and (b)), 680°C ((c) and (d)) and 700°C ((e) and (f)) respectively.

whiskers while the square ones denote the whisker density. From these results, it can be seen that the growth rate increases with increasing substrate temperature. The $ZrO_2$ whiskers have an average growth rate of 0.5 nm/s, 0.7 nm/s and 0.9 nm/s corresponding to the substrate temperature of 650°C, 680°C and 700°C, respectively. Furthermore, the whisker density decreases with increasing substrate temperature. At 650°C, the

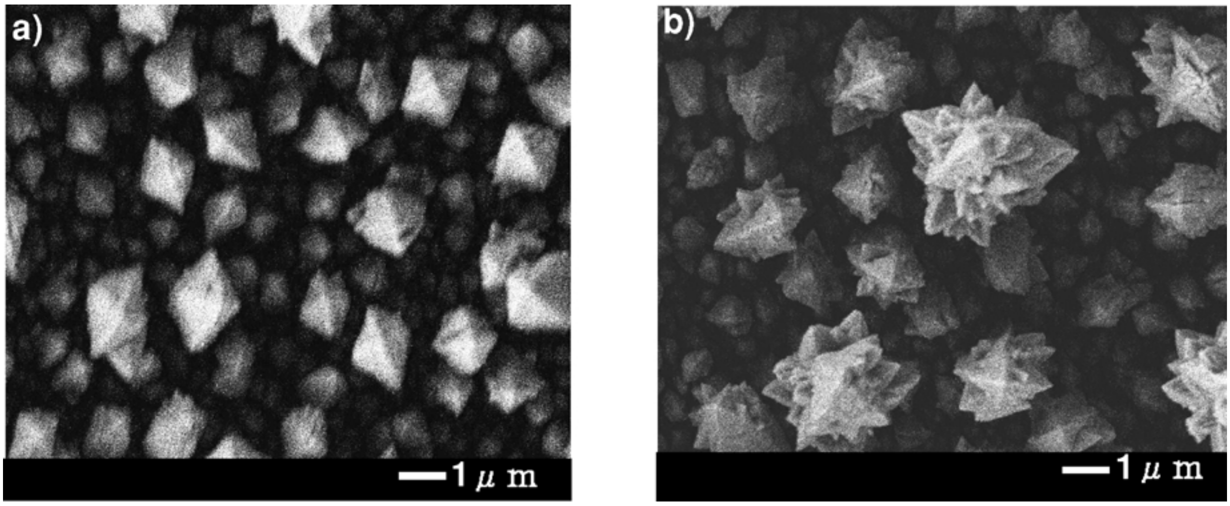

*Figure 4* Typical morphology of the whiskers synthesized at 700°C.

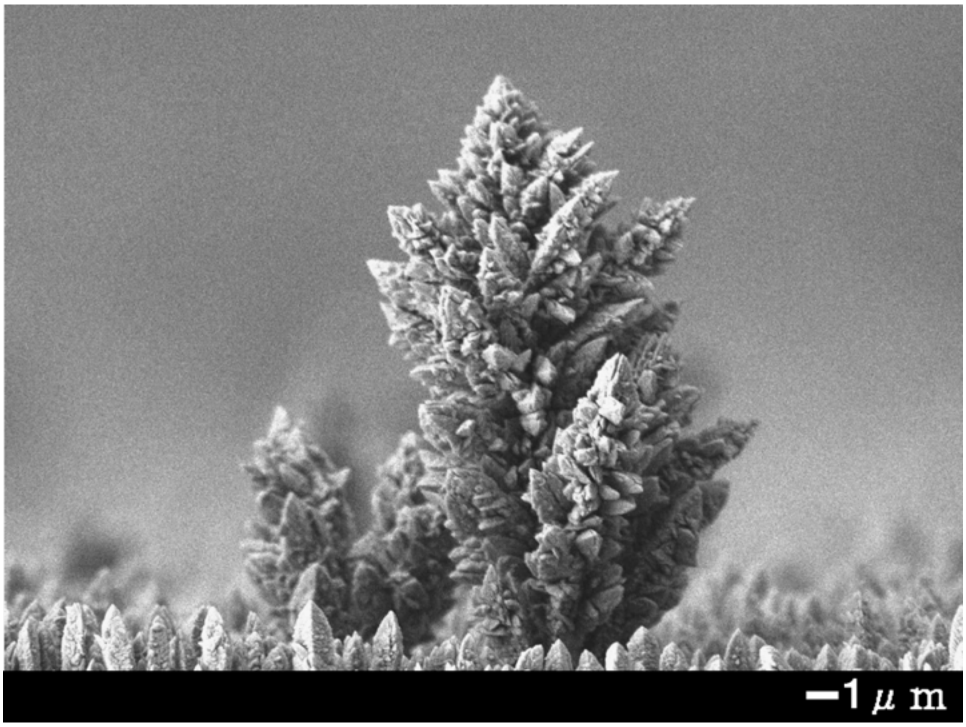

*Figure 5* SEM image of the dendrites seen on the whiskers synthesized at 700°C.

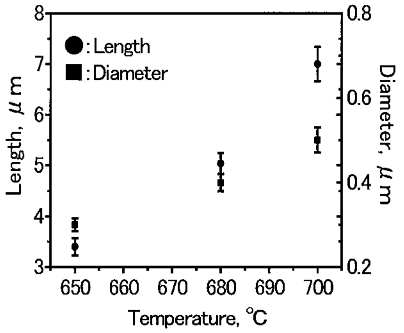

*Figure 6* Dependence of whisker length and diameter on substrate temperature.

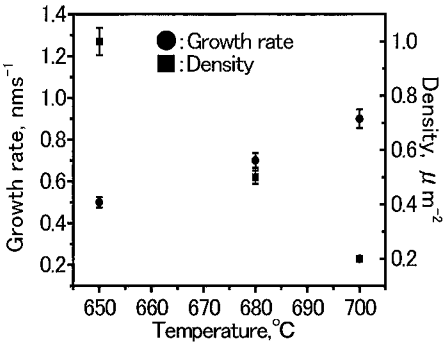

*Figure 7* Dependence of growth rate and whisker density on substrate temperature.

whisker density is $1/\mu\text{m}^2$ and drops sharply to reach the values of $0.5/\mu\text{m}^2$ and $0.2/\mu\text{m}^2$ at 680°C and 700°C, respectively. This drop of the whisker density led to the morphological instability of the crystallite and to the formation of dendrites in a few locations of the substrate as shown in Fig. 5. These dendrites grow relatively fast in comparison with the whiskers. They have an average growth rate of 4 nm/s. The formation of the whiskers and the dendrites seems to be a result of low supersaturation and intermediate supersaturation, respectively.

Since the grown whiskers have different morphologies, there might be some parameters or growth conditions affecting the whisker morphology. In order to clearly understand and control the morphology of the whiskers, the investigation of their growth mechanism is of high importance.

Two mechanisms of oxide growth are frequently examined: the vapor-liquid-solid or VLS process and the vapor-solid or VS technique [20]. The morphology of examined oxide whiskers ($ZrO_2$ whiskers in our study) is compared to that of the standard features observed in each growth mechanism. From the comparison, the suitable growth mechanism can be determined.

In whiskers grown by the VLS process, the liquid drop becomes supersaturated with the solid constituents and precipitation of the solid occurs. The liquid drop is sufficiently small so that no other nucleation occurs and growth continues on the single existing nucleus, the whisker. The characteristic feature of the VLS process is the presence of small droplets on the whisker tips at the end of the process.

The VS technique includes two different mechanisms. One mechanism of whisker growth is characterized by an anisotropic growth rate that is very fast in one crystallographic direction and leads to an elongated whisker. However, this mechanism requires a nucleation source and the whisker growth rate is limited by the gas solid interface reaction rather than by transport through the vapor. A possible site is ascertained by the presence of a screw dislocation at the substrate surface. In the second VS mechanism, if the whisker growth is limited by vapor transport. This can lead to a significant growth rate at the whisker tip because of the diffusion flux to the surface.

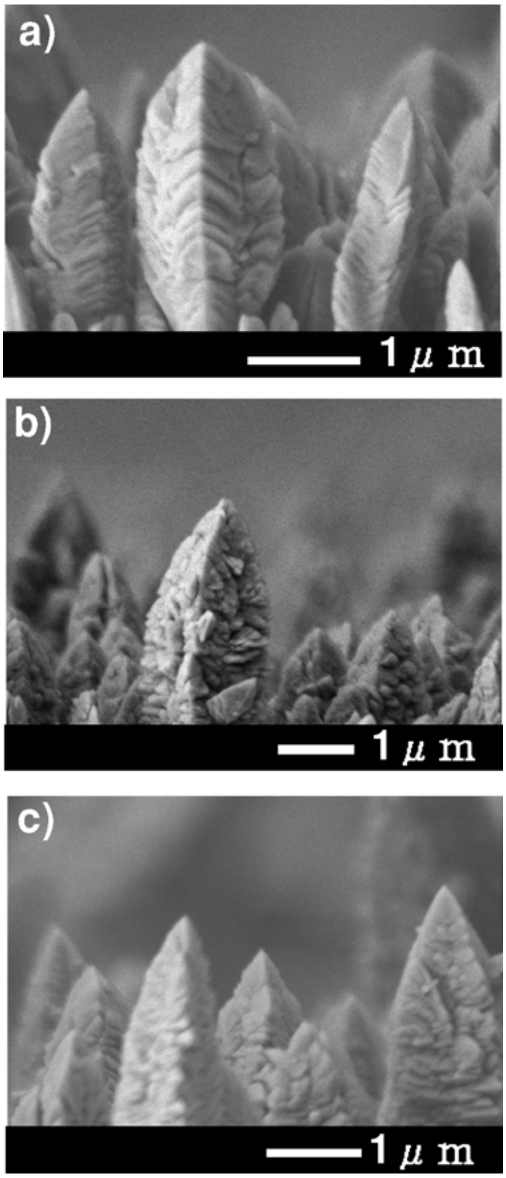

*Figure 8* SEM image of the whisker tips synthesized at various temperatures.

Fig. 8 shows the tips of whiskers synthesized at 650°C, 680°C, and 700°C, respectively. The characteristic feature of the VLS growth, indicated by the presence of small catalysis balls on the whisker tips, is not observed. In addition, there is no occurrence of a second phase, and the whiskers seem to grow along their preferred orientation. This indicates that the VLS process cannot be considered as the $ZrO_2$ whiskers growth mechanism in this study.

Furthermore, no screw dislocations have been observed at the substrate surface. This means that the VS growth mechanism that is characterized by an anisotropic growth rate, which is very fast in one crystallographic direction and leads to an elongated whisker cannot also be applied to describe the whisker growth in our study.

The whisker growth in this study seems to be limited by the vapor growth only. This means that the second VS mechanism is likely the most appropriate one in describing the $ZrO_2$ whisker growth.

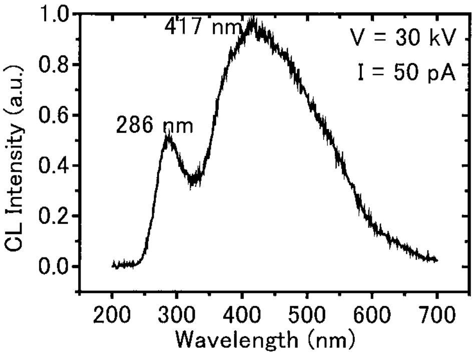

*Figure 9* CL spectrum for $ZrO_2$ whiskers synthesized at the substrate temperature of 700°C.

Finally, CL properties of the $ZrO_2$ whiskers were investigated. The CL spectrum for the $ZrO_2$ whiskers synthesized at the substrate temperature of 700°C is shown in Fig. 9. A noticeable CL emission can be observed in both the ultra-violet (286 nm) and the blue regions (417 nm). The existence of the emission in the blue region has already been reported [21] and it is attributed to the luminescence from intrinsic defects, as it is well known that $ZrO_2$ is a self-activated material. On the other hand, to our knowledge and according to the information available to us, the existence of the emission in the U.V. region is reported here for the first time. For the samples obtained at 650°C and 680°C, under the same measuring conditions (30 kV, 50 pA), the CL emission is hardly noticeable.

Although the obtained whiskers exhibit a good morphology, they still lack enough length to induce increase in fracture toughness. If this particular aspect is improved, $ZrO_2$ whiskers can find a possible application as reinforcement agents for both ceramic matrix composites and metal matrix composites. Furthermore, if the origin of the UV emission is elucidated, $ZrO_2$ whiskers can also find possible optical applications.

## 4. Conclusion

Homogeneous and oriented zirconium oxide whiskers were successfully synthesized by CVD technique operated under atmospheric pressure and the obtained results can be summarized as follows:

(1) The temperature appears to be the major factor affecting the whiskers morphology, size, growth rate and density.

(2) At a low substrate temperature, low supersaturation favors the whisker growth, while at higher substrate temperatures, intermediate supersaturation favors the formation of dendrites.

(3) The VS technique in which the whisker growth is limited by the vapor transport seems to be the appropriate mechanism for $ZrO_2$ whisker growth.

(4) A noticeable CL emission is observed in both the U.V. and blue regions, at room temperature.

## Acknowledgment

This work was fully supported by the Regional Consortium Project of the New Energy and Industrial Technology Development Organization (Japan).

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*Received 25 September 2002*
*and accepted 20 May 2003*