JOURNAL OF MATERIALS SCIENCE **39** (2004) 1683–1687

Surface morphological properties of sol-gel derived SiO_2 fiber

KYU-SEOG HWANG, JEONG-TAE KWON, JEONG-SUN OH
School of Automotive and Mechanical Engineering, Institute of Industrial Technology, Nambu University, 864-1 Wolgye-dong, Gwangsan-gu, Gwangju 506-824, Republic of Korea

JUN-HYUNG AN, BYUNG-HOON KIM*
Department of Materials Science and Engineering, Chonnam National University, 300 Yongbong-dong, Buk-gu, Gwangju 500-757, Republic of Korea
E-mail: bhkim@jnu.ac.kr

In this study, sol-gel derived SiO_2 fibers were prepared by mixing tetraethyl orthosilicate, ethanol, water and hydrochloric acid. Fibrous SiO_2 was drawn by using a viscous solution. Dried gel fibers were final heat-treated at 1000, 1100, 1200 and 1300°C for 1 h in air. Crystallinity of the SiO_2 fiber after annealing was measured by X-ray diffraction analysis. A field emission—scanning electron microscope and an atomic force microscope were used to evaluate surface properties. SiO_2 fiber heat-treated at high temperature, i.e., 1300°C, exhibited inhomogeneous surface structure.
© *2004 Kluwer Academic Publishers*

1. Introduction

The sol-gel process has widely been used as an alternative method to prepare a wide variety of applications including monoliths, powders, coatings and fibers. Among them, the basic rheologic properties of silica sols and the processing of sol-gel derived silica fibers have been studied widely [1–5].

By varying parameters such as catalyst, pH, solvent and water to metal alkoxide ratio, different gel structures are formed. The most common property of the sols in the fiber spinning is a low water-to-tetraethyl orthosilicate (TEOS) molar ratio (about 2). The low water-to-TEOS ratio indicates the formation of linear silica polymer, which is an important factor for the spinnable sols [6, 7].

In most cases, surface morphology of materials is of great importance for many technical applications requiring well-defined surfaces or interfaces. Hence a detailed knowledge of the roughness characteristics of the fiber will aid in the optimization of many parameters. Specially, in biological applications, such as bulks, coatings or fibers, surface topography and roughness are very important factors on *in vitro* bioactivity [8–11].

The objective of this experiment was to study the differences on the surface of sol-gel-derived silica fibers heat-treated at various temperature. An atomic force microscope (AFM) was used to monitor the surface topography and roughness of the heat-treated silica fibers. *In vitro* test was done by immersing in simulated body fluid (SBF).

2. Experimental procedure

SiO_2 fibers were prepared with starting solution from silicon alkoxide. Hydrochloric acid (HCl) was added as catalyst for the chemical reactions, and ethanol (C_2H_5OH) (EtOH) as the solvent. TEOS ($C_8H_{20}O_4Si$, MERCK, Germany) was first mixed in ethanol. The mixture was stirred for 60 min after which water and HCl mixed with an equal amount of ethanol were added. Then, the solution was poured into an evaporation dish at 80°C. Molar ratios of the ingredients used were TEOS:EtOH:H_2O:HCl = 1:2:2:0.07.

When the sol had become sufficiently viscose, spinnability tests were conducted by pulling fibers from the viscose sol with a glass bar. Then the sol fibers were placed back into the dry oven at 80°C in air until they became gel fibers. Gel fibers were converted to SiO_2 fibers by annealing at 1000, 1100, 1200 and 1300°C for 1 h in air (heating rate: 2–3°C/min). Fig. 1 shows flow chart of the experimental procedure.

A X-ray diffraction (XRD) (Rigaku Co., D-Max-1200, Japan) patterns of SiO_2 fibers were obtained with a CuK_α X-ray source at room temperature. A Field emission-scanning electron microscopy (FE-SEM) (S-4700, Hitachi, Japan) images of fiber's surface and cross-section area were taken. To monitor surface topography and roughness of the heat-treated SiO_2 fibers, AFM (Nanoscope Multimodel SPM, SPM-Digital Instruments, USA) was used. All images were recorded with a tapping mode AFM in air. Silicon cantilever with a resonance frequency of 250–300 kHz were used.

The *in vitro* formation of calcium phosphate (CaP) was evaluated by immersing the annealed fiber in

*Author to whom all correspondence should be addressed.

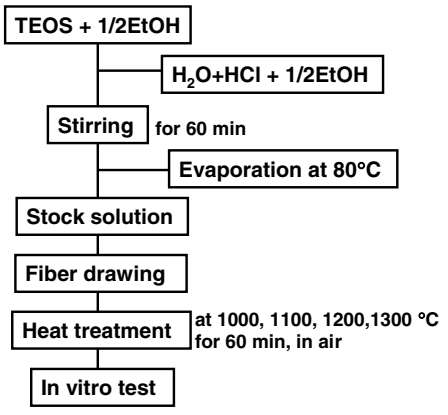

Figure 1 Flow chart of experimental procedure.

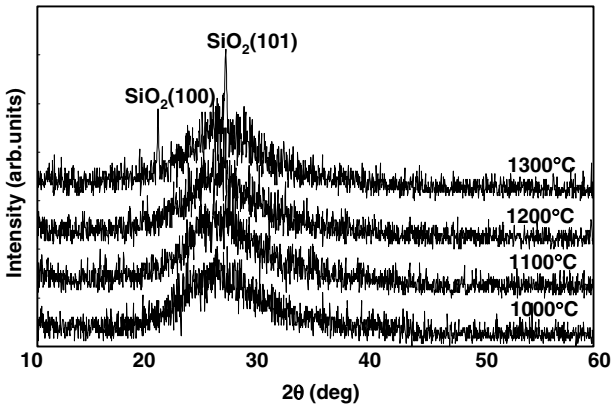

Figure 2 XRD patterns of SiO_2 fibers after annealing at various temperatures.

15 mL SBF for 5 days. SBF was prepared by dissolving NaCl, $NaHCO_3$, KCl, $K_2HPO_4{\cdot}3H_2O$, $MgCl_2{\cdot}6H_2O$, $CaCl_2$ and Na_2SO_4 in deionized water. To this solution, 50 mM tris-(hydroxymethyl) aminomethane $[(CH_2OCH_3)CNH_2]$ and 45 mM hydrochloric acid (HCl) were used as buffering agents to maintain the pH of SBF at 7.25 at 36.5°C [9].

The *in-vitro* test was performed in a constant temperature-circulating bath (Model 90, Poly Science, USA) at a temperature of 36.5°C. After immersion, the sample was removed from the SBF, carefully rinsed with distilled water, and dried at room temperature. FE-SEM and an energy dispersive X-ray spectroscope (EDS) was used to monitor variation of surface structure.

3. Results and discussion

Fig. 2 shows the XRD patterns of SiO_2 fibers after heat-treatment at various temperatures. Fibers heat treated at below 1200°C showed an amorphous structure. At 1300°C, the SiO_2 crystalline structure started to become visible with peaks corresponding to the (100) and (101) reflections at $2\theta = 20.7^\circ$ and 26.9°, respectively.

The FE-SEM images of the heat-treated SiO_2 fiber at 1300°C for 1 h were shown in Fig. 3. The shape of the fiber cross section is of circular type without fusion of fibers and the mean diameter of the fiber is about 70–80 μm. The dimensions and surface morphology of the samples thermally treated at 1000, 1100 and 1200°C were similar, i.e., about 40–80 μm, not shown here.

In order to more clearly elucidate surface roughness and morphology of the fiber according to annealing temperature, AFM analysis was performed. Fig. 4 shows the AFM images (1×1 μm) of the SiO_2 fibers after annealing at various temperatures. The smoothness of the surface of SiO_2 fibers after annealing at below 1200°C is very high. It is difficult to identify the formation of 3-dimensional out growth. However, SiO_2 fiber heat treated at 1300°C showed more rough surface structure than others annealed at lower temperature.

Fig. 5 shows AFM top-view images and surface roughness profile of SiO_2 fibers heat treated at various temperatures. SiO_2 fibers after annealing at below 1200°C showed very low root mean square (RMS) roughness, as shown in Fig. 5. Surface roughness of the SiO_2 fiber increased by heat-treatment at 1300°C, resulting in higher RMS roughness. In this case, we can conclude that increase of the surface roughness may be inducted by crystal growth of SiO_2 fiber, resulting in observable increase of RMS roughness.

Furthermore, we studied the surface roughness characteristics of SiO_2 fibers using power spectral density (PSD) curves obtained from AFM measurement. To investigate a larger PSD data, PSD curves obtained from combined AFM results, which were recorded over scan

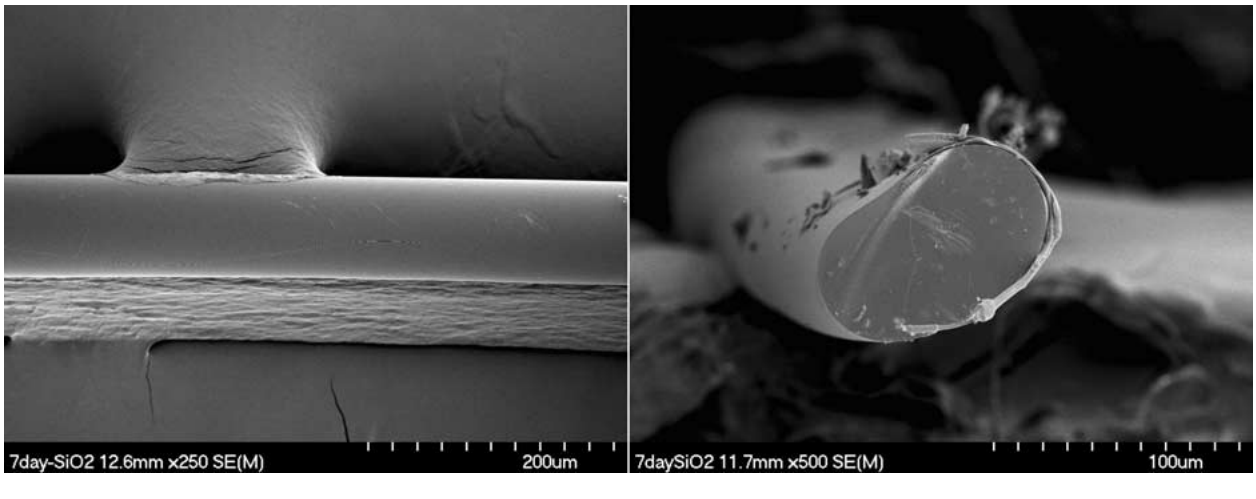

Figure 3 FE-SEM images of SiO_2 fiber heat-treated at 1300°C.

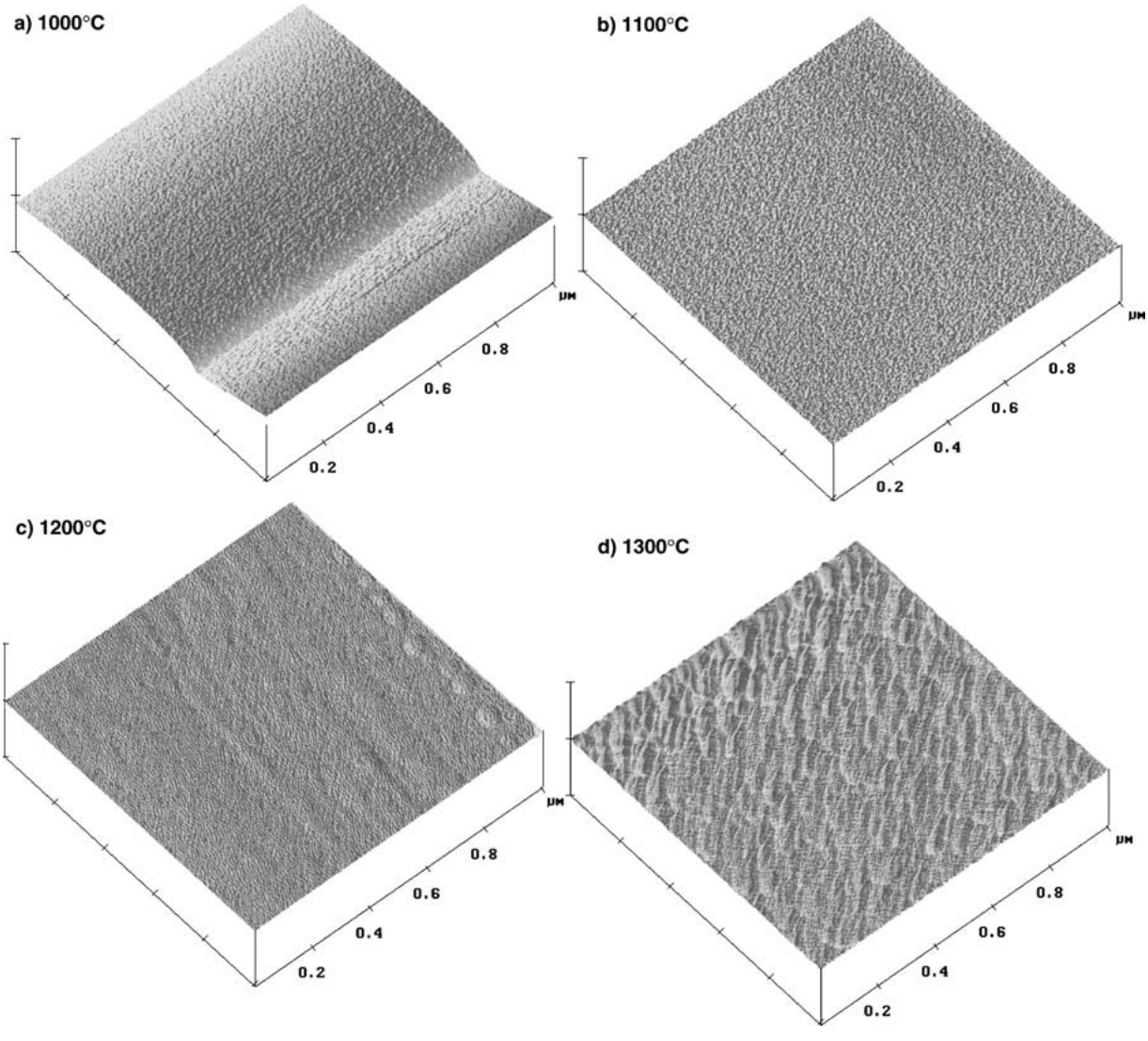

Figure 4 AFM images of SiO_2 fibers after annealing at 1000°C (a), 1100°C (b), 1200°C (c) and 1300°C (d).

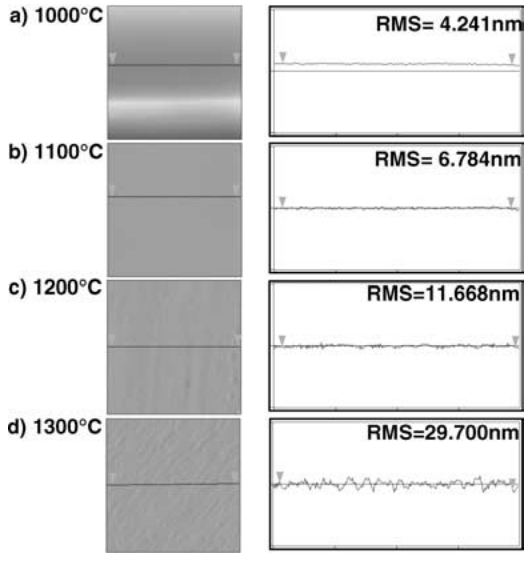

Figure 5 AFM top-view images and surface roughness profiles of SiO_2 fibers after annealing at 1000°C (a), 1100°C (b), 1200°C (c) and 1300°C (d).

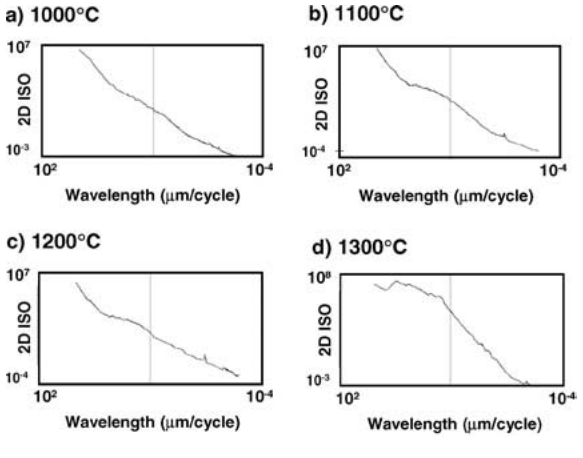

Figure 6 PSD curves of SiO_2 fibers after annealing at 1000°C (a), 1100°C (b), 1200°C (c) and 1300°C (d).

area from 0.1 μm × 0.1 μm and 1 μm × 1 μm to 8 μm × 8 μm, were presented.

When one is evaluating surface roughness, the PSD function is used increasingly as a valuable tool for topography description at surfaces, such as films [12]. While the RMS roughness as a single parameter of surface description reflects the standard deviation of all height values within the considered surface and does not provide any information on the topographical details of the surface, PSD curve can give the relative strength of each roughness component of a surface

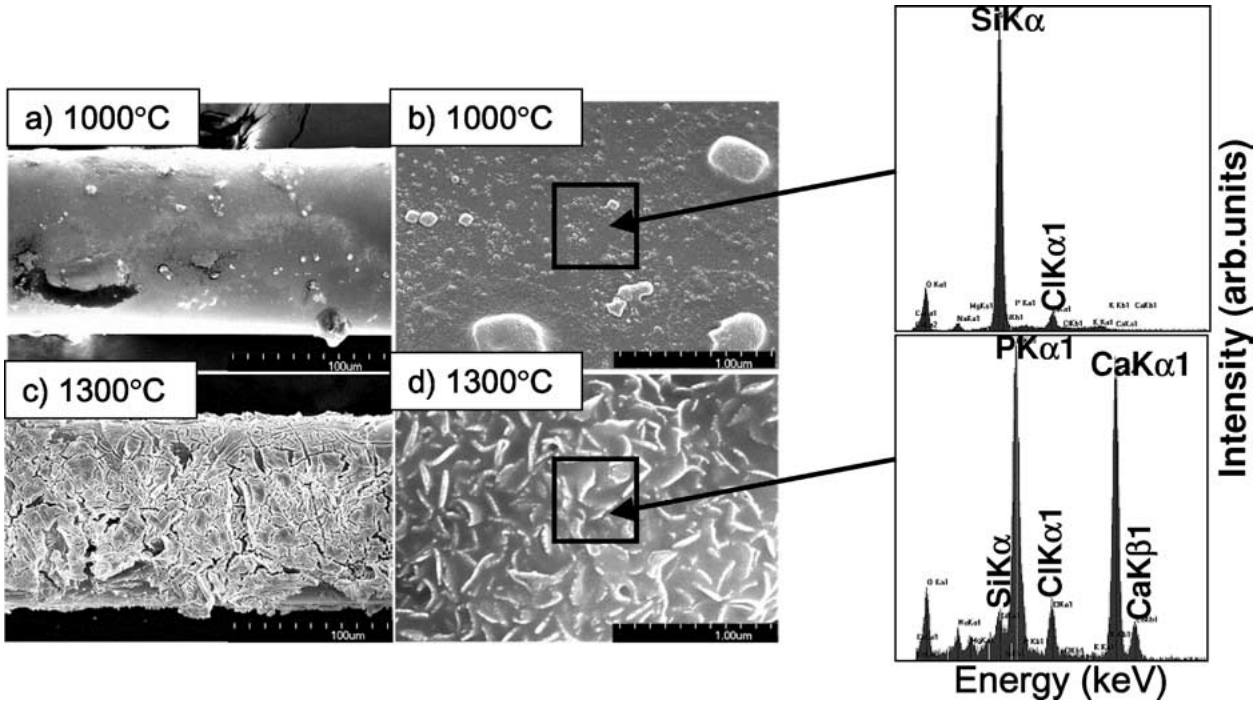

Figure 7 FE-SEM images and EDS spectra of the fibers annealed at 1000°C (a) and (b) and at 1300°C (c) and (d), after soaking for 5 days in SBF.

microstructure as a function of the spatial frequency [13].

Fig. 6 shows the result of PSD functions for the SiO_2 fiber after heat-treatment at various temperatures. For the fiber heat-treated at 1300°C, however, lower spatial frequency range in PSD curves was increased, resulting in linear-type PSD curves as increase of annealing temperature to 1300°C. At 1300°C, PSD curves of SiO_2 fiber revealed rough surface morphology, which could be attributed to the crystal growth as previously shown in XRD patterns and AFM images. Furthermore, for the fibers annealed at below 1200°C, its PSD curves showed much lower and broader shapes.

In biological applications, a general trend of the varying surface topography and its relation to *in vitro* bioactivity is shown in previous works [14]. The rougher the surface of the silica fibers, the better the bioactivity. Peltora *et al*. [14] suggested that the surface structure before immersion in SBF in the nanometer scale is the most important factor controlling the *in vitro* bioactivity of the heat-treated silica fibers. However, if better mechanical properties are needed, it is obvious that biodegradation of fibers is reduced due to denser structures, i.e., high-temperature annealing may have a negative influence on the biomaterials, by decreasing the surface reactivity, leading to a weaker bonding between the material and its host tissue.

However, as far as we know, there has been little information on the surface topography and bioactivity of sol-gel derived SiO_2 fibers heat-treated at high temperature, above ~1000°C, with dense structure. In our work, *in-vitro* test was performed on the samples annealed at 1000 and 1300°C after immersion for 5 days. As shown in Fig. 7, fully adsorbed crystals on sample annealed at 1300°C were identified after immersion for 5 days.

The calcium and phosphate ions required for hydroxy apatite generation on the surface were derived from the SBF. This was indicated by an increase of the formation of CaP on fiber (See Fig. 7). As clearly shown in Fig. 7, the sample annealed at 1300°C with relatively rough surface structure showed a CaP forming ability, while it is difficult to find CaP phase on the sample annealed at 1000°C.

The first step in the nucleation of hydroxy apatite in the presence of an osteoconduction oxide is thought to be an electrostatically driven adsorption of Ca^{2+} ions at ionized surface hydroxyl groups onto which phosphate is subsequently adsorbed [15].

Although SBF is supersaturated with respect to apatite [16], it is metastable because of the high energy required to form critical nuclei and the presence of inhibitors like Mg^{2+}. However, titania and silica gel prepared by sol-gel method can act as a stimulant to induce hydroxyapatite heterogeneous nucleation. Once apatite nuclei form, they grow spontaneously by taking the calcium and phosphate from SBF [9]. Certain hydroxyl groups, such as SiOH and TiOH, remaining in the sol-gel-prepared materials or absorbing during storage and immersion appear to promote hydroxyapatite generation by providing the sites for the CaP nucleation.

In our works, we assumed that a negatively charged layer by OH^- and relatively rough surface structure was probably responsible for CaP forming ability of sample.

4. Conclusions

Sol-gel derived SiO_2 fibers were prepared by mixing TEOS, ethanol, water and HCl. Gel fibers were converted to SiO_2 fiber by different thermal treatments at either 1000, 1100, 1200, and 1300°C for 1 h in air. Crystalline SiO_2 fiber heat-treated at 1300°C showed high RMS roughness and inhomogeneous surface structure by AFM analysis, while, for the amorphous SiO_2 fibers heat-treated at below 1200°C, low

RMS roughness and homogeneous surface were obtained. After soaking in SBF for 5 days, sample annealed at 1300°C having relatively rough surface structure showed a high CaP forming ability.

Acknowledgement

This study was supported by a grant of the Korea Health 21 R&D Project, Ministry of Health & Welfare, Republic of Korea (02-PJ3-PG3-31402-0006).

References

1. T. HASHIMOTO, K. KAMIYA and H. NASU, *J. Non-Cryst. Solids* **143** (1992) 31.
2. S. SAKKA and K. KAMIYA, *ibid.* **48** (1982) 31.
3. S. SAKKA and H. KOZUKA, *ibid.* **100** (1988) 142.
4. D. Y. SHIN and S. M. HAN, *J. Sol-Gel Sci. Tech.* **1** (1994) 267.
5. M. D. SACKS and R. S. SHEU, *J. Non-Cryst. Solids* **92** (1987) 383.
6. H. G. SOWMAN, *Ceram. Bull.* **67** (1988) 1911.
7. I. HASEGAWA, T. NAKAMURA, S. MOTOJIMA and M. KAJIWARA, *J. Non-Cryst. Solids* **8** (1997) 577.
8. T. KOKUBO, S. B. CHO, K. NAKANISHI, N. SOGA, C. OHTSUKI, T. KITSUGI, T. YAMAMURO and T. NAKAMURA, *Bioceram.* **7** (1994) 49.
9. S. B. CHO, K. NAKANISHI, T. KOKUBO, N. SOGA, C. OHTSUKI, T. NAKAMURA, T. KITSUGI and T. YAMAMURO, *J. Amer. Ceram. Soc.* **78** (1995) 1769.
10. M. JOKINEN, M. PÄTSI, H. RAHIALA, T. PELTOLA, M. RITALA and J. B. ROSENHOLM, *J. Biomed. Mater. Res.* **42** (1998) 295.
11. T. PELTOLA, M. JOKINEN, H. RAHIALA, M. PÄTSI, J. HEIKKILÄ, I. KANGASNIEMI and A. YLI-URPO, *ibid.* **51** (2000) 200.
12. J. M. ELSON and J. M. BENNETT, *Appl. Optics* **34** (1995) 201.
13. C. RUPPE and A. DUPARRÉ, *Thin Solid Films* **288** (1996) 8.
14. T. PELTOLA, M. JOKINEN, S. VEITTOLA, J. SIMOLA and A. YLI-URPO, *J. Biomed. Mater. Res.* **54** (2001) 579.
15. B. C. YANG, J. WENG, X. D. LI and X. D. ZHANG, *ibid.* **47** (1999) 213.
16. C. OHTSUKI, T. KOKUBO and T. YAMAMURO, *J. Non-Cryst. Solids* **143** (1992) 84.

Received 19 March
and accepted 3 October 2003