JOURNAL OF MATERIALS SCIENCE **40** (2005) 5641–5647

Laser fabrication and characterization of sub-millimeter joints between polyimide and Ti-coated borosilicate glass

DANIEL G. GEORGIEV*, TASLEMA SULTANA, AHSAN MIAN, GREG AUNER
Center for Smart Sensors and Integrated Microsystems, College of Engineering, Wayne State University, Detroit, MI 48202, USA
E-mail: dgeorgie@eng.wayne.edu

HANS HERFURTH, REINER WITTE
Fraunhofer Center for Laser Technology, 46025 Port St., Plymouth, MI 48170, USA

GOLAM NEWAZ
Center for Smart Sensors and Integrated Microsystems, College of Engineering, Wayne State University, Detroit, MI 48202, USA

Laser-fabricated joints of sub-millimeter widths between biocompatible, dissimilar materials have the potential for application as encapsulation of miniature implantable biomedical devices. In this work, we briefly describe the laser joining method of a very promising system, polyimide/titanium-coated borosilicate glass, and present results from characterization of such laser joints by means of mechanical failure (tensile) tests, optical and scanning electron microscopy, X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy. Our results suggest that the formation of the joints is a result of the creation of strong chemical bonds between Ti-containing species and certain polymeric functional groups. Mechanical tensile strength failure testing showed that such joints experience some degradation as a result of soaking in physiological solutions. This degradation is limited and, even after relatively long-term exposure the joints retain considerable strength. *© 2005 Springer Science + Business Media, Inc.*

1. Introduction

Development of new technologies for joining of materials, and dissimilar materials in particular, on a sub-millimeter and micrometer scale is of great importance to applications in a number of technological areas. Telecommunications/optoelectronics devices, microsystems technology (MST) and specifically micro-electro-mechanical systems (MEMS) and BioMEMS, combine components made of a variety of materials including silicon, polymers, glass, ceramics and metals. Device miniaturization is a major goal in MST. Upon miniaturization, portability is improved, the amount of required material is reduced, and the sensors reaction times are shortened. Cost reduction and improved performance are further advantages, however any further development of novel microsystems depends, at least in part, on the availability of assembly processes that allow high integration, hermetic sealing and automated processing with consistent high quality. The small size of the features, the heat sensitivity of integrated electronics and media, the precision alignment required to hold small tolerances, and the different materials to be joined represent major challenges in the assembly and packaging of such systems.

In the biomedical sector, new implantable microsystems have the potential to significantly impact the future treatment of diseases. Continuous advance in technology and medicine have resulted in a variety of implantable devices that are currently used for the treatment of a significant number of patients worldwide. The design of the encapsulation of advanced medical implants, such as devices that electrically stimulate and/or record neural activity, poses a number of serious requirements to the materials that are used. Among these requirements, biocompatibility and long-term stability are crucial. Often, the functionality of such devices requires the employment of dissimilar materials for which there are no reliable ways of joining that would also satisfy the need for biocompatibility and stability. Poor biocompatibility and lack of long-term stability, high heat input during soldering, and adhesive shrinkage during cure are indeed among

---

*Author to whom all correspondence should be addressed.

0022-2461
DOI: 10.1007/s10853-005-1291-6

the major drawbacks of the existing joining techniques. Such limitations can be overcome by laser joining techniques that intrinsically provide excellent focusing to spot sizes in the micrometer range, combined with precise control of the laser power in the focal spot to enable highly localized processing with minimum heat effect outside the joint region.

Recently we studied the nature of polyimide/bulk-Ti laser-fabricated joints, which were made in ambient conditions and our results gave evidence for a very sharp interface based on the creation of chemical bonds between Ti and O and C contained in polyimide [1]. Reactive metals like Ti are known to have low mobility in polymers and to form relatively sharp metal-polymer interfaces [2, 3]. Titanium is believed to interact primarily with the oxygen double bonded to carbon in the carbonyl groups >C=O, which form part of the polyimide (PI) molecular chains, and to form bonding configurations of the type Ti-O-C. XPS results have given evidence for the existence of TiO_2 particles [4] and Ti-C [5] bonds at such interfaces (obtained and examined under clean, vacuum conditions), and theoretical ab initio self-consistent-field calculations have identified chemical sites along the PI chains and mechanisms that favor the formation of such bonds [6]. According to our results, laser heating in ambient conditions also provides a mechanism for formation of joints based on strong chemical bonding between the surfaces of the Ti foil and the PI sheet.

The feasibility of laser joining PI to titanium and PI to titanium-coated glass has been investigated, and ranges of processing parameters that permit successful joining have been identified [7]. In order to understand the influence of the laser fabrication conditions on the joint quality and stability, we examined laser–fabricated joints between PI and titanium-coated borosilicate glass (BSG) by tensile mechanical failure (pull) tests, optical microscopy, scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and Raman spectroscopy. Such laser joints were also exposed to (soaked in) artificial cerebrospinal fluid (CSF) for different periods of time at 37°C in order to study any degradation effects caused by such a physiological solution.

2. Sample preparation and experimental conditions

PI sheet (Imidex, Westlake Plastics Company) was laser-joined to BSG (Pyrex 7740, Corning) coated with 0.2 μm-thick, sputtered Ti film by means of continuous wave radiation from a Yb-doped fiber laser at $\lambda = 1.1$ μm. A transmission joining configuration [7] was employed in which a clamping pressure of 200 MPa was used for the fabrication of the samples examined in this work. The laser beam with a total power of 1.0 W was focused on the Ti surface to a spot with diameter of 300 μm. A scanning speed of 100 mm/min was used to produce the joint line. PI is known to be transparent in the near-infrared region, and the PI sheet that we used was characterized by spectrophotometry and found to have a transmittance of 81% at $\lambda = 1.1$ μm.

Samples of the type described above with densely arranged parallel joint lines were also prepared for XPS measurements. These were separated into their PI and Ti parts by peeling in air and immediately introduced in the UHV-analysis chamber of a Perkin Elmer model 5500 XPS spectrometer. Both sides of the joint were studied. A relatively large analysis area was used that averaged over several joint lines and inter-joint regions following the procedure outlined in [1]. This approach was found to provide a good signal-to-noise ratio, and it insured that the signal was originating from a known area of the peeled joint. Thus all spectra that were obtained contained a ~50% contribution from the non-laser-treated surface of the sample, and the spectral analysis needed to take this into account. The base vacuum pressure was 5×10^{-10} Torr and an Ar-ion beam was used to sputter the sample surfaces in order to obtain spectra from various depths below the surface. A low-energy electron beam (neutralizer) was used to compensate for charging effects when studying the PI sheet (not needed in studying the Ti-coated glass plate).

Both the as-received and CSF-soaked laser joint samples were tested for mechanical tensile strength. The testing equipment used in this case consisted of a 6-axis micro-tester, which is a general-purpose micromechanical/thermal testing instrument. The machine was fully controlled by a computer, and could be operated both in displacement and load controls with six degrees of freedom [8], i.e., three orthogonal translations and three rotations. The displacement resolution of each closed-loop, DC-motor-drive stage was maintained at 0.1 μm in translations and 0.001 degree in rotations. A capacitance gage measured the displacement of the sample.

Scanning electron microscopy (SEM) images of the pull-test separated PI side and glass side parts of the joints were obtained in a Hitachi electron microscope, model S-2400. To avoid charging effects, the PI side part was sputter-coated with a thin Au layer prior to the SEM imaging.

Micro-Raman spectroscopy measurements were performed on laser-joint samples that were subjected to tensile mechanical testing and separated into their PI and glass parts. These experiments were done on a Renishaw InVia Raman microscope equipped with an Ar-ion laser emitting at $\lambda = 514.5$ nm and a diode laser emitting at $\lambda = 785$ nm. A 50× microscope objective was used to both deliver the excitation light and collect the Raman scattering signal (in a backscattering geometry), providing a spatial resolution of about 3 μm. The machine was fully controlled by a PC and was also equipped with a motorized high-precision XYZ microscope stage and a digital video camera allowing full control and documentation of the location from which the spectra were being collected.

3. Results and discussion

3.1. Tensile mechanical test results

The tensile mechanical test sample geometry is shown in Fig. 1a. Upon testing, samples were subjected to uniaxial tension (in-plane) by turning on the motor that moves in a direction perpendicular to the laser

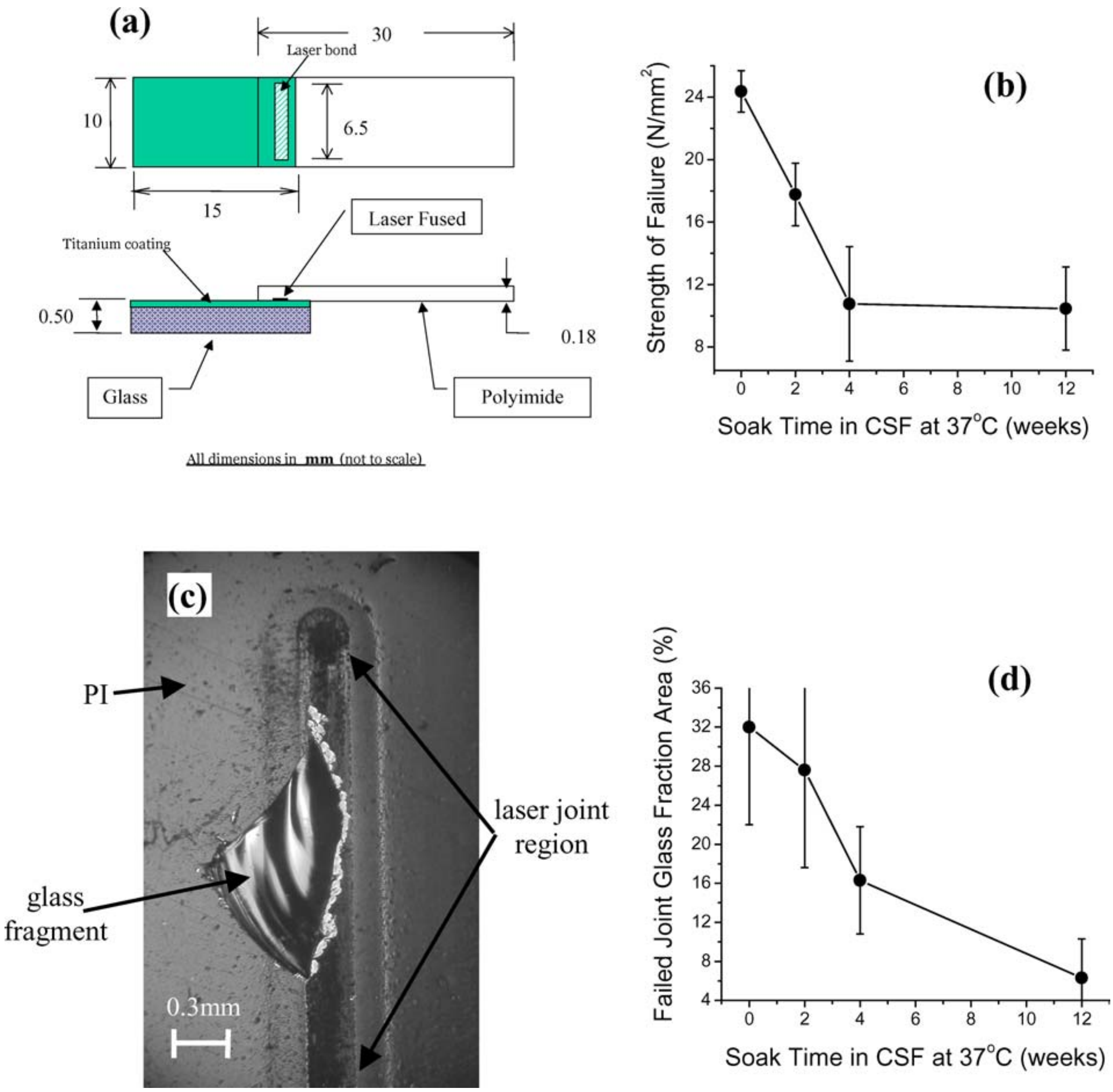

Figure 1 (a) Mechanical test sample configuration and sizes; (b) Strength of failure as a function of CSF soak time (at 37°C); (c) Optical microscopy image of a laser joint after tensile testing (polyimide side); (d) Glass-failure fraction of the failed laser joint area as a function of the CSF soak time.

joint. The software that controls the machine also acquires load cell and capacitance gage information (load-displacement data). The failure loads obtained for all samples were normalized by the joint area as measured by the optical microscopy. The test results are summarized in Fig. 1b. As can be seen, *the joint strength decreases during the first 2–4 weeks of exposure to CSF and then stabilizes at values that are about half as high as those of the as-received samples*. Despite this reduction in strength, the joints retain considerably high and stable strength values after such a long-term exposure to CSF.

Inspection of the failed joints under an optical microscope showed that the as-received samples (i.e., with no CSF treatment) failure occurred mostly in the glass and to a certain extent in the PI, but not at the interface. On the other hand, the CSF-soaked samples showed a more mixed mode of failure that included the glass, the PI and the interface (see Fig. 1c), with the fractions of the glass failure decreasing and the interface failure increasing with the soak time. Fig. 1d shows a plot of the glass-failure fraction of the failed laser joint area as a function of CSF-soak time.

Fig. 2 shows SEM images of the two parts of the laser joints after mechanical tensile-test failure. Shown are typical regions where failure occurred in the PI or at the interface (and not in the glass) of non-treated and CSF-soaked samples. It can be seen that the locus of failure of the original samples (non-treated) is away from the interface, deep in the PI (cohesive failure), causing large amount of PI residue on the glass side. In contrast, the failure of the CSF-soaked sample is much closer to (or at) the PI/Ti interface (interface failure) with little or no PI residue on the glass side, suggesting considerable weakening of the interface PI/Ti bonding as a result of the exposure to CSF.

3.2. XPS results

Both non-treated and 14-days-CSF-soaked (at 37°C) samples were studied. The CSF-soaked samples were rinsed in water and slowly dried after the exposure to

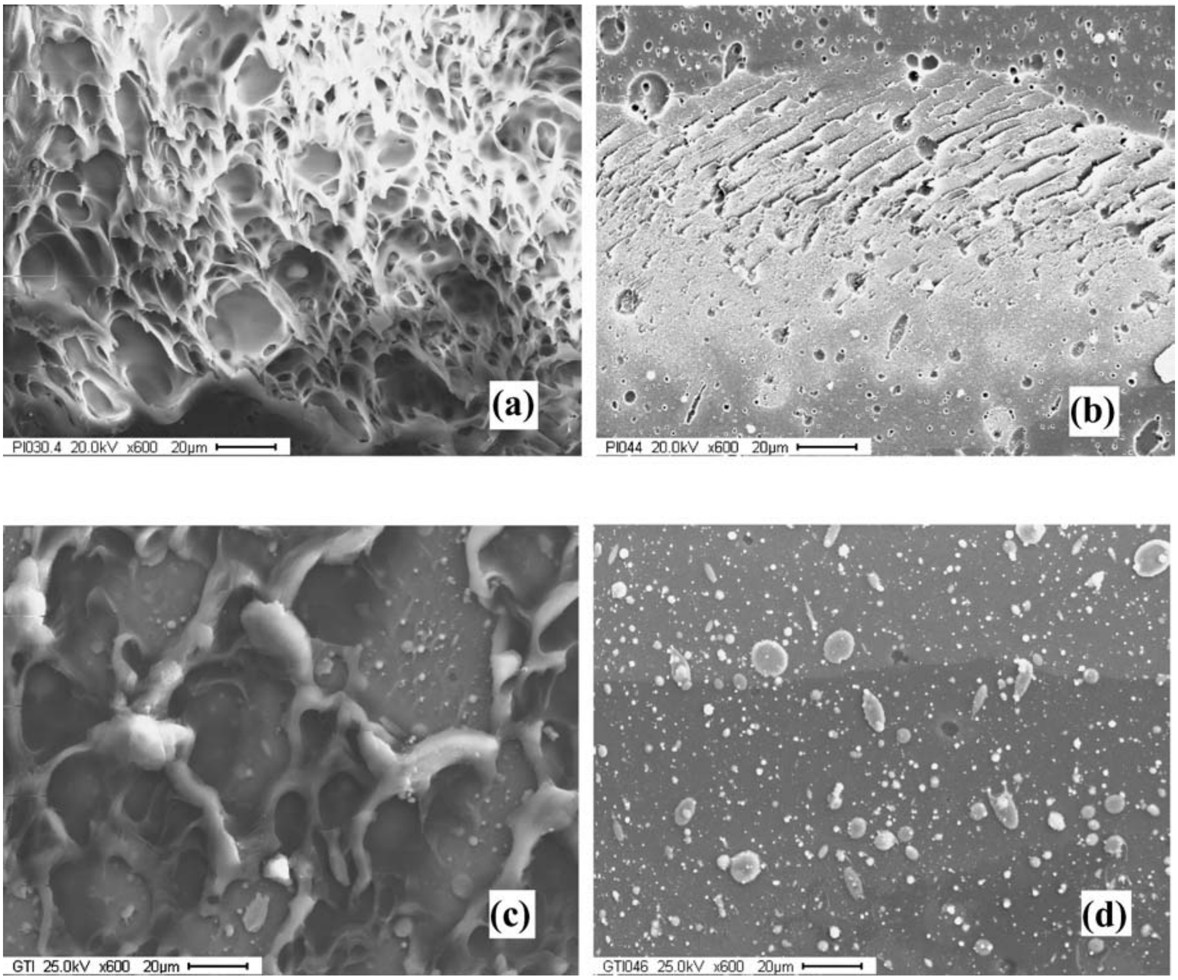

Figure 2 SEM images of pull-test-failed laser joint samples: (a) non-treated, PI side; (b) 12-week in CSF at 37°C, PI side; (c) non-treated, Ti-coated glass side; (d) 12-week in CSF at 37°C, Ti-coated glass side.

CSF and before the XPS characterization. There were no significant differences between the XPS spectra of the CSF-soaked and the non-treated samples. Apparently, the information that XPS can provide is not specific enough, or the sensitivity is not high enough, to reveal changes related to the joint interface degradation that resulted from this shorter-term (14 days) exposure to CSF. This degradation was otherwise evident from the mechanical tensile tests and the microscopy work described above. On the other hand, our XPS results provide important information about the structure of the PI/Ti interfaces that formed as result of the laser irradiation and heating during the joint fabrication process.

The PI/Ti-coated BSG laser joint interfaces can be expected to be similar or identical to those that form when laser-joining PI to bulk Ti plates [1]. Indeed that is what we observe and the XPS lineshapes of *the glass side* of a sample after peeling are shown below in Fig 3a and b. In both, the CSF-soaked and the non-soaked

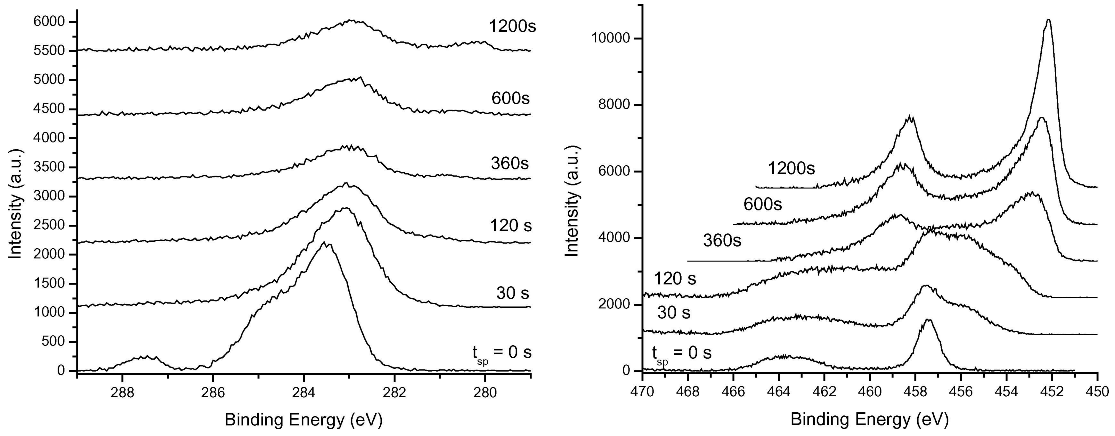

Figure 3 (a) XPS C 1s spectra from the "glass side" as a function of Ar-ion sputter time; (b) XPS Ti 2p spectra from the "glass side" as a function of Ar-ion sputter time.

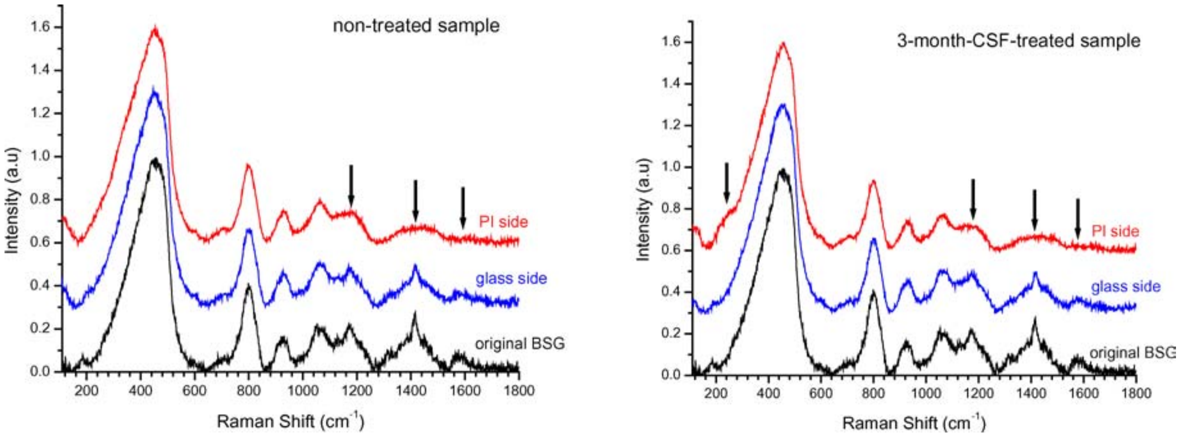

Figure 4 (a) Raman spectra of BSG in the laser joint region of as-received samples; (b) Raman spectra of BSG in the laser joint region of 3-month CSF-soaked samples.

sample cases *the PI side* did not contain any Ti which means that upon peeling the sample fails entirely within the PI plate (unlike the case of tensile testing failure, described above, where the samples fail in part in the glass substrate). Apparently, the mode of failure upon peeling is different from the one when tensile mechanical failure tests are preformed. The XPS C 1s line high-resolution (multiplex, Shirley baseline subtracted) spectrum is shown in Fig. 3a as a function of the depth of sputtering (i.e., sputtering time). At the surface (0 s sputtering, bottom), the spectrum corresponds to one from a PI surface with contributions from carbonyl groups (close to 288 eV) and other types of C environments that form the PI polymeric molecular structure [4, 5]. Upon sputtering the carbonyl group line disappears, the intensity (both total and relative to each other) of the other contribution changes, and, most significantly, a new line at around 281 eV, associated with Ti-C bonds, appears and becomes stronger (see especially the spectrum at 1200 s of sputtering).

The Ti 2p XPS spectra are shown in Fig. 3b. The spectra taken from the surface correspond to fully oxidized Ti, i.e., TiO_2. Deeper in the substrate, after 1200 s of sputtering (corresponding to a depth of 40–50 nm) the spectra consist almost entirely of pure metallic Ti: the 2p doublet is shifted downward by about 6 eV. Between these two extreme cases, we observe a mixture of states that evolve from pure oxide to pure metal with the increase of the sputtering time. These intermediate chemical states can be interpreted in terms of a mixture of oxidized states. Some of these states could be associated with Ti-C bonds that exist after 120 s of sputtering as revealed by the C1s spectra. The O1s XPS spectra (not shown) taken from the surface show several peaks, some of which come from the adsorbed oxygen at the surface and some from the TiO_2 and the PI. Upon sputtering, the adsorbed oxygen line disappears and only oxygen engaged in various Ti oxides is observed in agreement with what was described above for the C1s and Ti 2p XPS line cases.

3.3. Micro-Raman spectroscopy results

Typical Raman spectra of the BSG surface in the laser joint failure regions of as-received samples and 3-month CSF soaked (37°C) samples are shown in Fig. 4a and b, respectively. The baseline of the shown spectra was subtracted and then they were normalized to the intensity of the strongest peak. Also shown in these figures (bottom) is the spectrum of the original bulk BSG (Corning Pyrex 7740) taken under identical conditions. The second spectrum in each graph is taken from the exposed glass surface of the glass plate side of the failed (during a tensile mechanical strength measurement) laser joint sample. The top spectra in the graphs are taken from the exposed surface of glass fragments that were found on the PI side of the failed sample (such as the one shown in Fig. 1c). These fragments represent regions of the laser joint where the joint failed in the glass volume and not at the very interface or in the PI volume. In these fragments the PI/Ti interface is preserved and is covered with (a thin layer of) glass, the spectrum of which is shown in the topmost position in each graph in Fig. 4.

As it can be seen from Fig. 4a, the glass side spectrum is almost identical to the one of the original glass. On the other hand, the spectrum from the PI side (top) shows some differences and these are indicated by arrows in the graph. The weak band around 1600 cm^{-1} is almost absent in the PI side spectrum and so is the very sharp peak at 1410 cm^{-1} (B-O stretching modes region [9]) while the peak at 1180 cm^{-1} (Si-O stretching modes region [9]) has considerably lower intensity. These differences in the spectra indicate changes in the molecular structure of the glass in the glass fragments with respect to the original bulk glass. If the structure of the glass is altered locally and/or defects are introduced, it can be expected that the glass will become weaker in the affected region and that region would be the one to fail in a mechanical strength test. The glass fragments on the PI side represent such altered regions as a result of the *laser joint fabrication process* (*i.e. of the heat generated by the laser beam*).

The spectra of the 3-month CSF soaked laser joint samples (Fig. 4b) are similar to those of the as-received ones and *show very few additional differences with respect to the original glass*. The PI side spectrum shows all the differences (with respect to the original glass) that are observed in the spectrum of the as-received PI side. The only new change here is the weak elbow at about 250 cm^{-1} that accompanies the main band at 450 cm^{-1}. The origin of this feature is not clear to us at this time.

As it became evident from the mechanical tensile testing and optical microscopy studies, after exposure to CSF the laser joints failure occurs predominantly in the PI. Therefore, Raman spectra of the PI surfaces could, in principle, provide further insight into the reasons for the partial mechanical weakening of the laser joints as result of exposure to CSF. We were able to obtain micro-Raman spectra of the original PI material and the PI side of non-treated and CSF-treated, separated laser joints by using the $\lambda = 785$ nm excitation radiation. Unfortunately, in all cases, the spectra were virtually identical and we could not draw any conclusion as far as the degradation of the joints is concerned. Apparently, any changes that might have occurred in the PI material (whether due to the laser joining or to the CSF exposure), did not affect a significantly deep layer, so most of the Raman signal was collected from an unaltered volume around the joints, resulting in spectra indistinguishable from those of the original PI material. Surface-enhanced Raman spectroscopy techniques might be of help in the Raman characterization of this type of samples.

3.4. Discussion

Our interpretation of the results is that the joint degradation mechanism is primarily due to CSF-induced *weakening of the PI at the PI/Ti interface in the joint region.* The glass in the proximity of the interface region seems to be largely unaffected by the CSF-soak which is also supported by the Raman results. Polyimide is permeable to water and the absorbed water in the PI sheet (as a result of the soak) can reach the interface with the Ti coating. The bonding between PI and the Ti coating is due to Ti-O and Ti-C chemical bonds (with both the O and the C atoms being part of the original PI polymeric surface) created during the laser fabrication process [1]. Most generally, the Ti-O bonds are not stable and the absorbed water additionally oxidizes these units leading to the formation of stable TiO_2. This would reduce the bonding at the interface and would result in the observed decrease in the laser joint strength (Fig. 1b). Similarly, in earlier work, the peel strength degradation of PI/Ti interfaces (obtained by vacuum deposition of Ti on PI) upon hydrothermal cycling had been shown to result from water absorption and oxidation reactions at the interface [10]. The hydrothermal cycling degradation of interfaces between PI and other metals had also been studied and the mechanism of degradation had been attributed to water absorption in PI and water-induced oxidation at the interface [11, 12]. We assume that Ti-C bonds are more stable and remain largely intact preserving some of the bonding at the interface which would explain the considerable residual strength of the joints after longer soaking time (Fig. 1b). In view of Fig. 1d, samples that were not soaked show a mixed mode of failure: the locus of failure is in the glass or in the polyimide or at the very interface apparently because of the comparable strength of all these parts of the laser joint. After soaking, the PI and the interface are weakened and we see less and less failure in the glass.

To verify the assumption that water absorption is the main reason for the observed degradation in our case, we performed a 2-week soak test with the same type of samples, using distilled water instead of CSF and keeping all other test parameters unchanged. Indeed, the tensile failure tests results on these water-soaked samples showed a relative decrease in the failure strength which was comparable to that in the 2-week CSF-soaked samples (Fig. 1b).

4. Conclusions

Biocompatible joints between polyimide and titanium-coated borosilicate glass with good long-term stability in physiological solutions and sub-millimeter width were fabricated by a novel laser technique. XPS characterization of such joints gave evidence for the formation of strong chemical bonds between Ti-containing species and certain polymeric functional groups. Raman spectroscopy results revealed some changes in the molecular structure of the borosilicate glass as a result of the laser fabrication process. These changes can be correlated with a general weakening of the glass in the joint region which is responsible for the failure of untreated laser joint samples upon tensile mechanical testing. The Raman results did not show significant changes in the glass as a result of a 3-month CSF soak. Based on our results, the observed, limited joint strength degradation in CSF solution can be attributed water-induced weakening of the laser joint interface, probably due to further oxidation of unstable Ti suboxide species.

Acknowledgements

We acknowledge helpful discussions with Ronald J. Baird. This work was supported by the Michigan Life Sciences Corridor Grant GR-358.

References

1. D. G. GEORGIEV, G. NEWAZ, G. AUNER, H. J. HERFURTH and R. WITTE, *Appl. Surf. Sci.* **236** (2004) 71.
2. F. FAUPEL, R. WILLECKE, A. THRAN, M. KEINE, C. VONBECHOTOLSHEIM and T. STRUNSKUS, *Defect Diff. Forum* **143** (1997) 887.
3. N. MARIN and Y. SERRUYS, *Nucl. Instr. Meth. Phys. Res B* **131** (1997) 109.
4. C. GIRARDEAUX, E. DRUET, P. DEMONCY and M. DELAMAR, *J. Electron. Spectrosc. Relat. Phenom.* **70** (1994) 11.
5. F. S. OHUCHI and S. C. FRELICH, *J. Vac. Sci. Technol. A* **4** (1986) 1039.
6. C. GIRARDEAUX, G. CHAMBAUD and M. DELAMAR, *J. Electron. Spectrosc. Relat. Phenom.* **77** (1996) 209.
7. I. BAUER, U. A. RUSSEK, H. HERFURTH, R. WITTE, S. HEINEMANN, G. NEWAZ, A. MIAN, D. GEORGIEV and G. AUNER, in Proceedings of SPIE—Photonics West LASE 2004: Lasers and Applications in Science and Engineering Conference, 24–29 January 2004, (SPIE Press, San Jose, California, 2004) Vol. 5339, p. 454.

8. A. MIAN, G. NEWAZ, L. VENDRA, M. RAHMAN, D. G. GEORGIEV, G. AUNER, R. WITTE and H. HERFURTH, *J. Mater. Sci. Mater. Med.* (accepted)
9. T. FURUKAWA and W. B. WHITE, *J. American Ceramic Soc.* **64** (1981) 443.
10. A. C. CALLEGARI, H. M. CLEARFIELD, B. K. FURMAN, T. G. GRAHAM, D. NEUGROSCHL andS. PURUSHOTHAMAN, *J. Vac. Sci. Technol. A* **12** (1994) 185.
11. B. K. FURMAN, K. D. CHILDS, H. CLEARFIELD, R. DAVIS and S. PURUSHOTHAMAN, *ibid.* **10** (1992) 2913.
12. D.-Y. SHIH, N. KLYMKO, R. FLITSCH, J. PARASZCZAK and S. NUNES, *ibid.* **9** (1991) 2963.

Received 26 February
and accepted 31 March 2005