



## XPS analysis of laser transmission micro-joint between poly (vinylidene fluoride) and titanium

Taslema Sultana<sup>a,b,\*</sup>, Grigor L. Georgiev<sup>a,b</sup>, Greg Auner<sup>c</sup>, Golam Newaz<sup>b,d</sup>, Hans J. Herfurth<sup>e</sup>, Rahul Patwa<sup>e</sup>

<sup>a</sup> Department of Chemical Engineering and Materials Science, 5050 Anthony Wayne Drive, Detroit, MI 48202, USA

<sup>b</sup> Institute for Manufacturing Research, Wayne State University, 666 Hancock Avenue, Detroit, MI 48202, USA

<sup>c</sup> Department of Electrical and Computer Engineering, 5050 Anthony Wayne Drive, Detroit, MI 48202, USA

<sup>d</sup> Department of Mechanical Engineering, 5050 Anthony Wayne Drive, Detroit, MI 48202, USA

<sup>e</sup> Fraunhofer Center for Laser Technology, 46025 Port Street, Plymouth, MI 48170, USA

### ARTICLE INFO

#### Article history:

Received 26 October 2007

Received in revised form 12 June 2008

Accepted 28 July 2008

Available online 3 August 2008

#### Keywords:

Transmission laser micro-joining

Ti/PVDF interface

XPS

Ti–F

Ti–C

### ABSTRACT

Micro-joints between poly (vinylidene fluoride) (PVDF) film and titanium (Ti) foil with a joint width of 250  $\mu\text{m}$  were fabricated by a transmission laser joining technique. The Ti and PVDF surfaces exposed by debonding the joint were studied by X-ray photoelectron spectroscopy (XPS). The XPS results suggest that laser joining leads to the formation of Ti–F and Ti–C chemical bonds at the interface.

© 2008 Elsevier B.V. All rights reserved.

## 1. Introduction

Localized joining of dissimilar materials, particularly polymeric materials, is of great importance in packaging of miniaturized micro-electronics, telecommunications, and optoelectronics devices. With conventional joining technologies for joining of dissimilar materials such as soldering, adhesive bonding and ultrasonic welding, which are area bonding techniques, it is difficult to produce localized joints. Localized joining of dissimilar materials can be achieved by transmission laser joining. The focused laser beam defines the position and size of the joint, and the controlled heat input decreases the possibility of thermal damage to sensitive components. Flexibility, shorter processing time, consistent quality and repeatability are the other advantages of laser joining. In transmission joining, the joining material combination includes one material that is absorbent and one that is transparent at the laser wavelength. The laser energy is directed through the transparent part, and it is

absorbed at the surface of the absorbing part, thus allowing the heat to be selectively delivered to the interface.

Poly (vinylidene fluoride) (PVDF) is a flexible polymer, which has a high piezoelectric coefficient, and low acoustic and mechanical impedance. These properties make the PVDF a very desirable material for micro-electro-mechanical systems (MEMS) applications. PVDF is also biocompatible. It is a biomaterial established for soft tissue applications and as a suture material [1]. It is chemical and weather resistant, durable and has very low water absorption. PVDF can be considered as a potential material for application in biomedical devices [2]. Although PVDF possesses many desirable properties, it is known that the adhesion and bonding of metals to this polymer is difficult, because of the inert surface of the polymer. Earlier studies show that reactive metals (such as Cr, Ti, Ta and Al) react extensively with fluoropolymer surfaces, whereas inert metals (such as Cu, Ag and Au) do not. Reactive metals, particularly chromium and titanium interact strongly with polymers and form sharp and thermally stable interfaces [3]. Several studies have been conducted on metal/PVDF interfaces fabricated by evaporation of the metal onto the polymer surface. It was found that there is a formation of organometallic species at the interface. The evaporation of Ni onto the PVDF surface leads to chemical bond formation between the metal and

\* Corresponding author at: Institute for Manufacturing Research, Wayne State University, 666 Hancock Avenue, Detroit, MI 48202, USA. Tel.: +1 313 577 3692; fax: +1 313 577 8789.

E-mail addresses: [taslema@wayne.edu](mailto:taslema@wayne.edu), [sumi94@yahoo.com](mailto:sumi94@yahoo.com) (T. Sultana).

the carbon from the  $-\text{CF}_2-$  group of the polymer. The results show evidence for the formation of nickel fluoride and new carbon containing products (a combination of  $-\text{CFNi}-$  and graphite like carbon). The carbon from the  $-\text{CH}_2-$  group of the polymer was unaffected by Ni [4]. The interfaces between PVDF and vapor deposited Cr and Ni metal films were studied by another group. They also reported the formation of carbide and fluoride species on the substrates [5].

Transmission laser joining has been used to successfully join dissimilar materials such as polymers to metals or polymers to metal film coated glass [6–10]. The average shear strength of the laser joint of Ti/PVDF system (described system in this paper) is 6.7 MPa. This is comparable to the average adhesive joint strength (steel/PVDF/steel) of PVDF film which was found to be 5.1 MPa [11]. Earlier studies conducted by our group on other laser joining systems like titanium/polyimide give evidence for the formation of chemical bonds between the polymer and Ti [12,13]. Since the laser joints are fabricated in ambient conditions, the natural oxide layer on the Ti surface affects the chemical bond formation so that in fact Ti-oxide/PVDF interfaces were fabricated. In this paper, the interactions between Ti and PVDF due to laser joining will be discussed. X-ray photoelectron spectroscopy (XPS) will provide an insight into the chemical interactions between the Ti and PVDF polymer that occurs during the laser joining process.

## 2. Sample preparation and experimental conditions

A continuous wave (cw) Yb-doped fiber laser ( $\lambda = 1100$  nm) (JDS Uniphase Inc.) having a Gaussian beam power profile was used in the bonding processes. The laser joined samples were prepared at the Fraunhofer Center for Laser Technology (CLT), Plymouth, MI, USA. PVDF film (Kynar 460, Atofina Chemicals Inc) of 0.13 mm thickness was laser-joined to 0.05 mm Ti foil (99.99% purity, Goodfellow Corp.) by using a laser power of 4.5 W and a scanning speed of 180 mm/min. A 0.05 s initial dwell time was used during the sample preparation to preheat the starting point and make joint lines with uniform width. A clamping pressure of 415 kPa was used in the joining procedure to hold the sample between two borofloat glass plates (11 mm thick). A thin cork sheet with a nickel plate of 0.5 mm thickness on top of it was placed between the bottom glass block and the sample to work as a damper to even out any pressure difference on the sample through the Ti film. The details of the transmission laser joining can be found in the references [6,12]. The materials were ultrasonically cleaned with acetone and iso-propanol and then dried with nitrogen gas before joining. The laser beam is first focused on the Ti surface at the interface, and then it is defocused by the desired distance to get a joint width of 0.25 mm. The defocusing of the beam controls the joint width and reduces overheating and burning of the polymer by lowering the intensity in the center of the laser spot.

A PVDF/Ti sample with multiple laser joints of the type shown in Fig. 1 was prepared. The length of the laser joints was measured to be 6.5 mm. The total widths of the laser joints were measured to be 0.75 mm (0.25 mm actual bond width plus 0.50 mm heat affected zone) and the space between joints was 0.25 mm. The surface that was analyzed thus contained  $\sim 25\%$  contribution from the actual bond,  $\sim 50\%$  contribution from the heat affected zone and  $\sim 25\%$  contribution from the non-laser-treated surface of the sample. The XPS data were collected in the UHV-analysis chamber of a PerkinElmer model 5500 XPS spectrometer using monochromatized AlK $\alpha$  excitation. The base vacuum pressure was  $6 \times 10^{-10}$  Torr. An analyzer pass energy of 23.5 eV was used in the case of the high resolution (multiplex) spectra. The data were collected from a 2 mm diameter area thus averaging over two joint

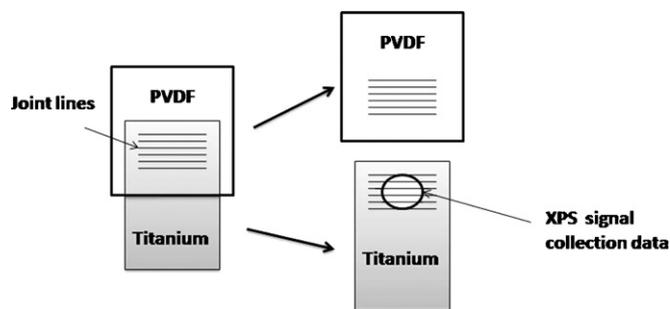


Fig. 1. Schematic diagram of a XPS sample.

lines. The joined samples were separated into their plastic and metal parts by peeling in air. An Ar-ion beam was used to sputter the sample surfaces in order to obtain spectra from various depths below the surface. A beam voltage of 4 kV and raster size of 4 mm  $\times$  4 mm was used during sputtering. A low-energy electron beam (neutralizer) was used to compensate for charging effects when studying the polymer surface. The binding energy scales were adjusted using the C1s line at 284.6 eV. The spectra were not modified by the smoothing procedure. The curve fitting was done by fitting a Gaussian–Lorentzian mixture function (the mixture ratio was 90:10) to the experimental data using a curve-fitting program, AugerScan3, supplied by RBD Instruments, Inc. The variation of the full width at half-maximum (FWHM) for the peaks was maintained at  $1.5 \pm 0.1$ . The curve fitting was preceded by Shirley integrated baseline subtraction. Sensitivity factors ( $S$ ) for the C1s, O1s, Ti2p3, and F1s core level spectra were  $S(\text{C1s}) = 0.296$ ,  $S(\text{O1s}) = 0.711$ ,  $S(\text{Ti2p3}) = 1.198$ , and  $S(\text{F1s}) = 1.00$ .

## 3. Results and discussion

### 3.1. XPS survey spectra

The XPS survey spectrum of the PVDF surface of the peeled joint showed mostly carbon and fluorine and a small amount of oxygen. There was no evidence for Ti on the PVDF surface. The survey spectrum of Ti surface was dominated by Ti2p and O1s peaks with a strong C1s and a detectable N1s peak. The F1s was below the noise level in survey spectrum, but it was observed in narrower scans with better statistics. In the XPS signal collection area as shown in Fig. 1, there is no gross evidence of PVDF residue. It is

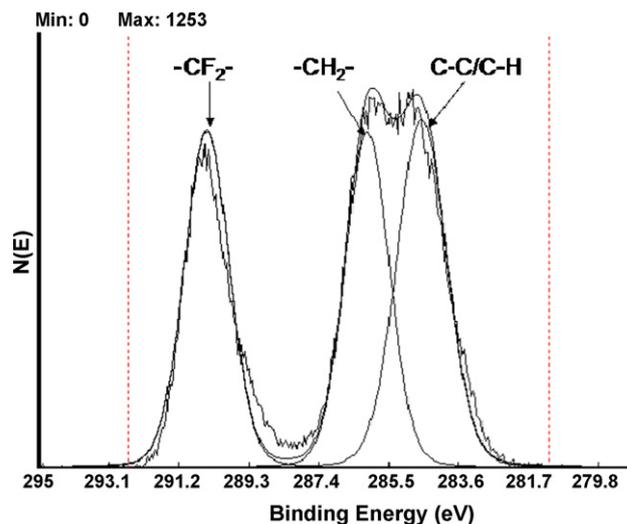


Fig. 2. C1s XPS spectrum taken from PVDF.

likely that a small, unknown fraction of the XPS signal is coming from a very thin PVDF residue in the interface region.

### 3.2. PVDF C1s spectrum

The PVDF C1s spectrum (Fig. 2) consists of three components – peaks at 286.1 eV due to carbon bonded to hydrogen in the polymer and a peak at 290.4 eV from carbon bound to two fluorines in the polymer [14] and a peak at 284.6 eV. The ratio of the  $-\text{CH}_2-$  and  $-\text{CF}_2-$  components in PVDF was nearly 1:1 as estimated from the XPS intensities. The peak at 284.9 eV is probably due to adventitious carbon.

### 3.3. XPS of Ti surface

#### 3.3.1. C1s spectra

The XPS C1s spectrum taken from the surface of the Ti side of the PVDF/Ti sample is shown in Fig. 3. The spectrum can be resolved into six peaks with some at relatively high binding energy indicating that the carbon species are in a very electronegative environment. The major peak at 284.6 eV is again most likely due to adventitious carbon. The peaks at 286.4 eV, 288.0 eV and 289.3 eV are likely from PVDF residue bound to the surface. Similar to the PVDF surface, the peaks at 286.4 eV and 289.3 eV are likely to originate from the  $-\text{CH}_2-$  and  $-\text{CF}_2-$  components in PVDF respectively. The peak at 288.0 eV is consistent with carbon bound to single electronegative atom such as fluorine or oxygen from the  $\text{TiO}_2$ . The ratio of the  $-\text{CH}_2-$  and  $-\text{CF}_2-$  components of the C1s spectrum is about 0.4. This observation is consistent with dehydrohalogenation of PVDF which is a known thermal degradation mechanism for PVDF [15]. The loss of HF from adjacent carbons will decrease the number of  $-\text{CF}_2-$  groups and give rise to  $-\text{CF}=\text{CH}-$  groups. The peak at 288.0 eV is too intense to be accounted for by the  $-\text{CF}=\text{CH}-$  groups and it probably has some contribution from oxygenated species.

The peaks at 292.6 and 295.2 eV are in the region associated with  $-\text{CF}_3$  and  $-\text{O}-\text{CF}_3$  groups seen in perfluorinated ethers. These high binding energy species may be associated with carbon bound to multiple fluorine and oxygen atoms at the  $\text{TiO}_2$  surface. The XPS C1s XPS spectra taken from the Ti side of the sample during a series of sputter etchings are shown in Fig. 4. After 30 s of sputtering, the peaks in the range from 290 eV to 284 eV have been significantly reduced, and the peaks at 292.6 and 295.2 eV are shifted to 293.7 eV and 296.4 eV, respectively.

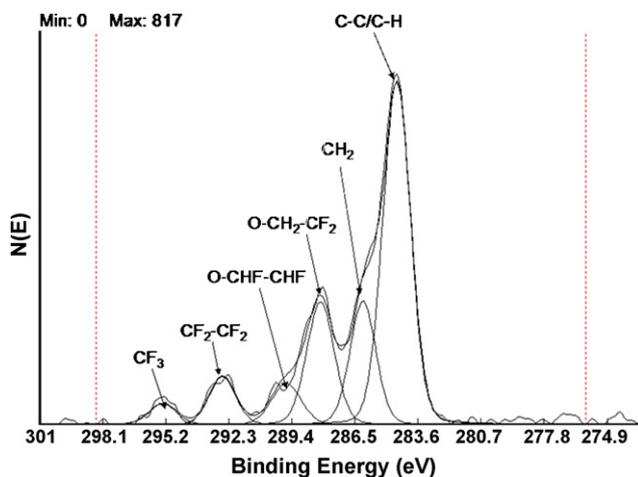


Fig. 3. C1s XPS spectrum taken from the Ti side of the sample.

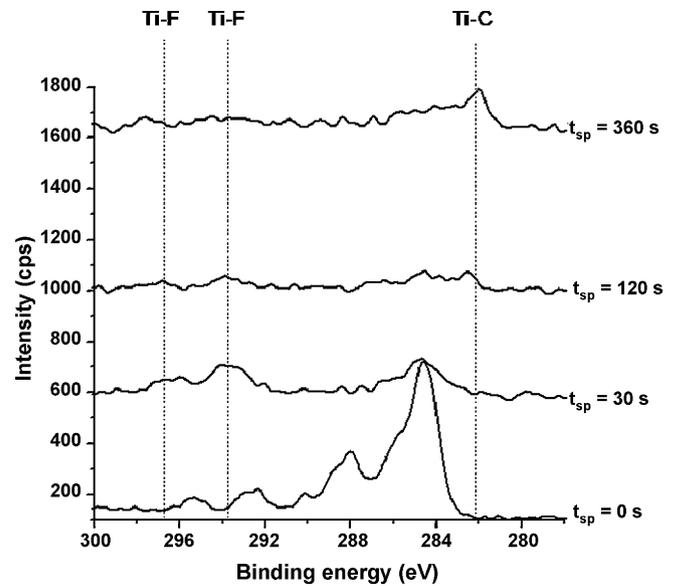


Fig. 4. C1s XPS spectra taken from the Ti side of the sample after sputtering for the indicated times.

This suggests that the polymer related carbonaceous layer on the surface is thin, and that the species giving rise to the high binding energy peaks are tightly bound to the surface. After sputtering for 120 s the high binding energy peaks are attenuated and a new feature is emerging at 282.2 eV. This new peak gains intensity after sputtering for 360 s. The binding energy of 282.2 eV peak is close to the value for the C1s line in TiC reported in the literature [12,16]. However, this peak is not seen initially and it increases with continued sputtering. It is not possible to say with certainty whether the TiC like species was formed at the interface of the polymer/ $\text{TiO}_2$  interface during bonding, or whether it was formed by ion induced reaction of the carbon with the  $\text{TiO}_2$  surface.

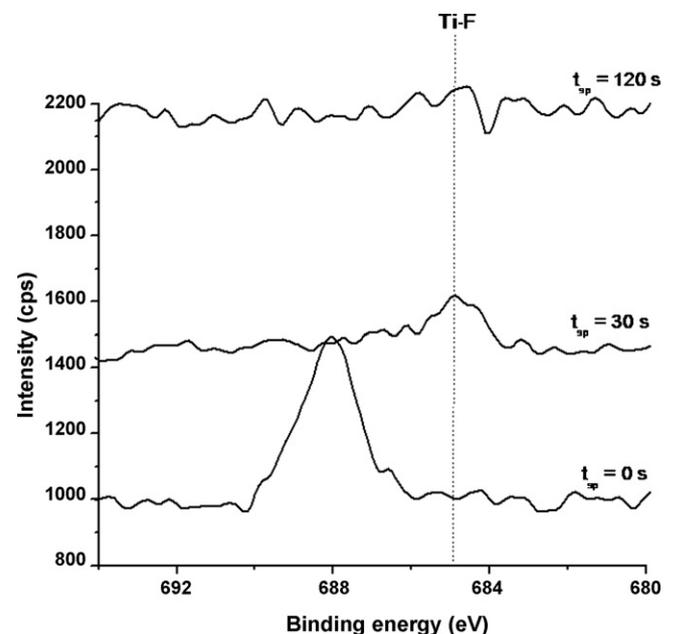


Fig. 5. F1s XPS spectra taken from the Ti side of the sample after sputtering for the indicated times.

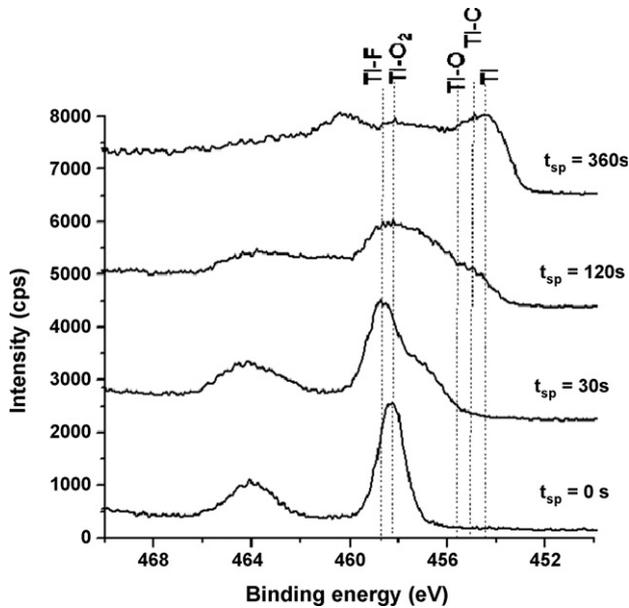


Fig. 6. Ti2p XPS spectra taken from the Ti side of the sample after sputtering for the indicated times.

### 3.3.2. F1s line

F1s spectra taken from the Ti side of the sample during a sputtering series are shown in Fig. 5. The F1s line at the surface consists of a peak at 688 eV, which corresponds to the fluorine from the polymer chain. After sputtering for 30 s the peak which corresponds to the fluorine from the polymer disappears and a new peak at 685 eV appears. The peak at 685 eV is consistent with compounds such as  $\text{TiF}_3$  or  $\text{TiF}_4$  [17]. The absence of this 685 eV peak in the spectrum of the unspattered surface and the two high binding energy peaks in the C1s spectrum of the unspattered surface indicate that fluorine on the unspattered surface is bound to carbon. After sputtering for 30 s both the carbon and fluorine associated with the polymer are removed. The remaining carbon and fluorine have binding energies consistent with carbides and fluorides respectively. These species may exist at the polymer/oxide interface and indicate chemical reaction during bonding, or they may be artifacts due to ion beam induced reactions during sputtering. The spectrum taken after sputtering for 120 s does not show the presence of fluorine.

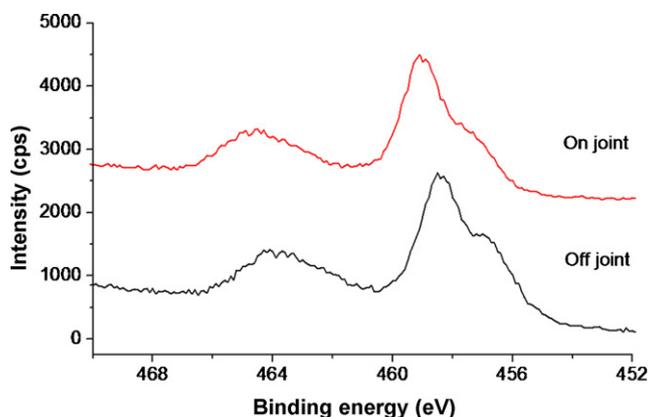


Fig. 7. Comparison between the Ti2p spectra taken from the Ti part of the sample and the non-treated Ti foil taken after 30 s of sputtering.

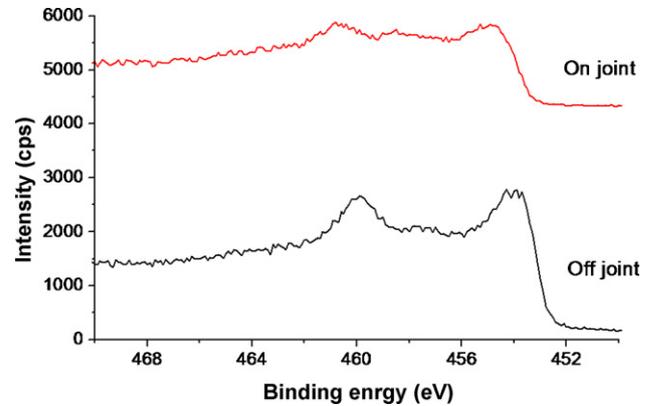


Fig. 8. Comparison between Ti2p spectra taken from the Ti side of the sample and the non-treated Ti foil after 360 s of sputtering.

### 3.3.3. Ti2p line

Fig. 6 shows the evolution of the Ti2p spectra taken from the Ti side of the sample during sputtering. The spectrum taken from the surface consists of  $\text{TiO}_2$  with a  $\text{Ti}2p_{3/2}$  binding energy of 459.0 eV. As stated above, most of the signal ( $\sim 75\%$ ) is obtained from the non-bonded Ti foil. With sputtering, the Ti2p peaks broaden and shift to lower binding energy. This is typical behavior for  $\text{TiO}_2$  (and other reducible oxides) in which metal oxide is reduced to a sub-oxide. This beam induced reduction makes it difficult to directly interpret the sputter series on  $\text{TiO}_2$ . Therefore it is useful to compare spectra from the joint area with comparable spectra taken off of the joint area. Fig. 7 makes such a comparison after 30 s of sputtering. The  $\text{Ti}2p_{2/3}$  peak is at a noticeably higher binding energy in the spectrum taken on the joint. A component with a higher binding energy in the Ti2p spectrum and the shift of the fluorine 1s spectrum to lower binding after 30 s of sputtering are both consistent with the formation of titanium fluoride species on the treated Ti foil. In Fig. 8 a comparison between the Ti2p spectra taken from the Ti

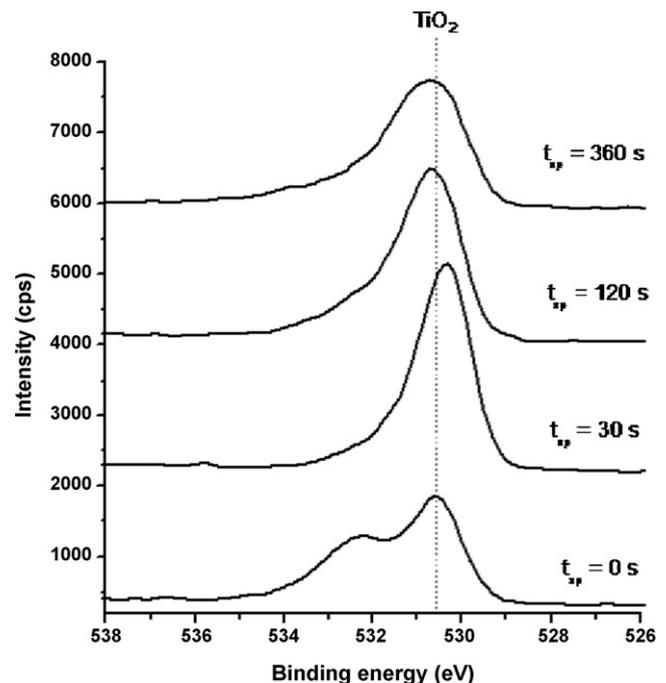


Fig. 9. O1s XPS spectra taken from the Ti side of the sample after sputtering for the indicated times.

side of the sample and the non-treated Ti foil after 360 s of sputtering is shown. The peaks are broad and unresolved. The major difference between these spectra is that the valley between the spin-orbit doublet is shallower in the spectrum taken on the joint. The binding energies for titanium suboxides and titanium carbide are similar, but the presence of another species would be expected to broaden the unresolved peak envelope.

#### 3.4. O1s line

The O1s XPS spectra taken from the Ti side of peeled joint are shown in Fig. 9. The spectrum taken from the surface of the Ti side of the laser joint consists of two peaks: main component at 530.7 eV, which can be assigned to oxygen from the natural TiO<sub>2</sub> layer of the Ti foil and a second peak at 532.5 eV, which can be attributed to surface species such as hydroxides. Upon sputtering for 30 s, the peak at 532.5 eV disappears and the oxygen intensity increases due to removal of the carbonaceous layer. With continued sputtering, the O1s peak intensity decreases as oxygen is preferentially removed from the surface and the peak broadens indicating a variety of chemical environments on the ion beam reduced surface.

#### 4. Conclusions

PVDF film and an oxidized Ti foil were joined by a transmission laser joining technique. The interface of the joint was studied by XPS and optical microscopy. The results of these experiments suggest that the locus of failure of the joint is in the polymer layer just below the interface. There is clear evidence of modified PVDF on the titanium foil surface and some suggestion of Ti–F and Ti–C bonding. The laser joining process may lead to the formation of chemical bonds between the Ti and PVDF film, and these chemical bonds may contribute to the strength of the laser micro-joint of the Ti/PVDF system

#### Acknowledgments

We would like to acknowledge the assistance of Dr. Erik McCullen in performing the XPS measurements and Prof. Ronald J. Baird in interpreting the XPS results. This work was supported by Michigan Economic Development Corp. (MEDC) (grant # 06-1-P1-0219).

#### References

- [1] D. Klee, Z. Ademovic, A. Bosserhoff, H. Hoecker, G. Maziolis, H.-J. Erli, *Biomaterials* 24 (2003) 3663.
- [2] M. Tanaka, Y. Tanaka, S. Chonan, *Journal of Intelligent Material Systems and Structures* 19 (2008) 35.
- [3] F. Faupel, R. Willecke, A. Thran, C.v. Bechtolsheim, M. Kiene, T. Strunskus, *International Congress on Adhesion Science and Technology*, Amsterdam, 1995.
- [4] T.C.S. Chen, S.M. Mukhopadhyay, *Journal of Applied Physics* 78 (9) (1995) 5422–5426.
- [5] F.M. Pan, J.L. Huang, C.F. Liaw, *Journal of Vacuum Science and Technology A* 11 (6) (1993) 3076–3080.
- [6] I. Bauer, U.A. Russek, H. Herfurth, R. Witte, S. Heinemann, G. Newaz, A. Mian, D. Georgiev, G. Auner, in: *Proceedings of SPIE – Photonics West LASE 2004: Lasers and Applications in Science and Engineering conference*, San Jose, California, 2004.
- [7] H. Herfurth, R. Witte, S. Heinemann, G. Newaz, A. Mian, D. Georgiev, G. Auner, in: *Proceedings of the 23rd International Congress on Applications of Lasers and Electro-Optics (ICALEO 2004)*, San Francisco, California, 2004.
- [8] G. Newaz, D. Georgiev, A. Mian, G. Auner, R. Witte, H. Herfurth, *Laser in Proceedings of the MRS Fall Meetings*, Boston, MA, 2004.
- [9] A. Mian, G. Newaz, J. Vendra, N. Rahman, D. Georgiev, G. Auner, R. Witte, H. Herfurth, *Journal of Materials Science: Materials in Medicine* 16 (3) (2005) 229–237.
- [10] A. Mian, T. Sultana, G. Auner, G. Newaz, *Surface Interface Analysis* 39 (6) (2007) 506–511.
- [11] T. Sultana, Ph.D. Dissertation, 2007, Wayne State University, Detroit, p. 172.
- [12] D.G. Georgiev, R.J. Baird, G. Newaz, G. Auner, R. Witte, H. Herfurth, *Applied Surface Science* 236 (2004) 71–76.
- [13] D. Georgiev, T. Sultana, A. Mian, G. Auner, R. Witte, H. Herfurth, G. Newaz, *Journal of Materials Science* 40 (2005) 5641–5647.
- [14] M.D. Duca, C.L. Plosceanu, T. Pop, *Journal of Applied Polymer Science* 67 (1998) 2125–2129.
- [15] B.-E. El Mohajir, N. Heymans, *Polymer* 42 (2001) 5661.
- [16] L. Ramqvist, K. Hamrin, G. Johansson, A. Fahlmann, C. Nordling, *Journal of Physics and Chemistry of Solids* 30 (1969) 1835–1847.
- [17] F. Fracassi, R. d'Agostino, *Pure and Applied Chemistry* 64 (1992) 703.