Applied Surface Science 258 (2012) 5052–5055

Contents lists available at SciVerse ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

# Fabrication of micro-structures on a PVDF/$TiO_2$ nano-composite film using photocatalytic lithography

Ningli An[a], Hongzhong Liu[a,*], Yucheng Ding[a], Bingheng Lu[a], Min Zhang[b]

[a] State Key Laboratory for Manufacturing Systems Engineering, Xi'an Jiaotong University, Xi'an 710049, China
[b] College of Chemistry & Chemical Engineering, Shaanxi University of Science & Technology, Xi'an 710021, China

ARTICLE INFO

*Article history:*
Received 4 November 2011
Received in revised form 18 January 2012
Accepted 18 January 2012
Available online 26 January 2012

*PACS:*
82.65.+r
83.80.Tc

*Keywords:*
PVDF
$TiO_2$
Micro-structure
Photocatalytic
Degradation

ABSTRACT

In the present study, a poly(vinylidene fluoride) (PVDF)/$TiO_2$ nano-composite film was prepared by coating a substrate with an acetone/DMF solution, which was then evaporated at a temperature of 110 °C. Micro-structure patterns were fabricated on a PVDF/$TiO_2$ nano-composite film with photocatalytic lithography. The morphological and chemical compositions of the micro-structure were investigated by optical microscope, SEM and XPS. Experimental results show that the micro-structure patterns can be directly replicated on the PVDF/$TiO_2$ nano-composite film with photocatalytic lithography. The micro-structure is approximately 4 μm in depth which is obtained during the water phase of the process with UV-LED irradiation in 5 h. The results indicate that the fabrication methodology can be potentially applied towards the large-scale fabrication of actuators and sensor devices.

## 1. Introduction

For several decades, there has been extensive research on the development of PVDF piezoelectric polymers, which can carry out expanding or contracting actions after electrical stimulation or detect changes in loading or environmental conditions. PVDF has significant application potential for actuators and sensors because of its desirable properties, such as the material's mechanical flexibility, light weight, biocompatibility, and simplicity of fabrication. However, there is a difficulty in integrating ferroelectric PVDF thin films into device applications during the manufacturing process.

PVDF is well-known for its complicated polymorphism, and different processing conditions will result in different polymorphisms. The β phase PVDF is desirable for its good piezoelectric properties. To achieve the integration of β phase PVDF with microelectromechanical systems (MEMS), some studies focused on obtaining β phase PVDF on the silicon substrate without stretching the polymer, in which clay, hydrated ionic salt or PMMA were blended with the PVDF polymer [1–4]. However, these studies only focused on the material's performance, while the fabrication of pattern structure was not mentioned. While it is necessary to fabricate specific PVDF pattern structures for application in MEMS devices through etching, the traditional etching process has a high probability of destroying the surface of the PVDF film by removing the protective photoresistance layer. Hence, nondestructive etching on a PVDF surface is another critical barrier to its use in MEMS.

In the past few decades, $TiO_2$ has been extensively studied [5,6] as a photocatalyst for the acceleration of the photodegradation of polymers in some research studies [7–10]. The degradation mechanism is based on the fact that $TiO_2$ contains electrons which can be excited by visible light frequencies to form electron–hole pairs. In the presence of water and oxygen, electron–hole pairs could produce highly reactive radicals which can oxidise polymers [11–13], as shown in Fig. 1(a).

In our previous work, a PVDF/$TiO_2$ electroactive film was prepared by coating a substrate with an acetone/DMF solution which was evaporated at a high temperature to obtain the desired PVDF β phase, resulting in a high dielectric constant and an electric breakdown field [14]. As $TiO_2$ can catalyse the degradation of PVDF when irradiated with UV rays, the photocatalytic lithography method can be used to fabricate the patterns on the film in large batches to lower the cost. In the present study, we fabricate the grating structure on the PVDF film surface during the water phase of the process with UV-LED irradiation.

---

* Corresponding author. Tel.: +86 29 83395021; fax: +86 29 83399508.
*E-mail address:* hzliu@mail.xjtu.edu.cn (H. Liu).

0169-4332/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.apsusc.2012.01.103

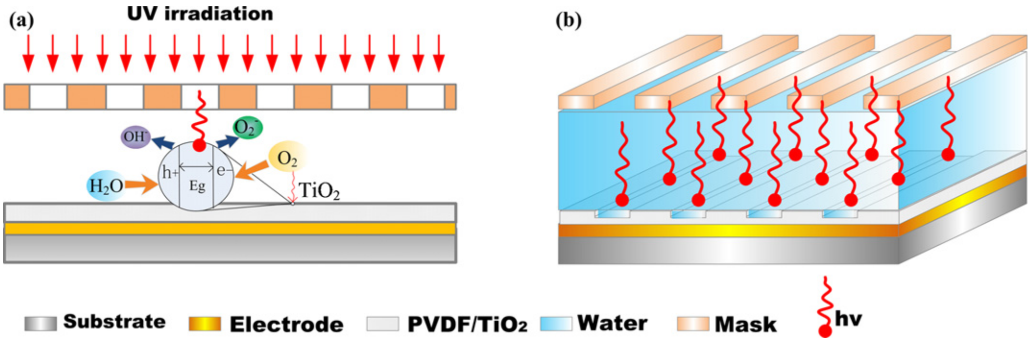

**Fig. 1.** A schematic diagram of micro-structure fabrication on PVDF/$TiO_2$ films with UV photocatalytic lithography. (a) Photoreaction processes at the $TiO_2$ surface and (b) UV irradiation during the water phase of the process.

## 2. Experiments

### 2.1. Material preparation

PVDF powder was obtained from the Sigma–Aldrich Corporation (Saint Louis, Missouri, USA). $TiO_2$ nano-particles (Degussa P25) with a mean diameter of 21 nm were mixed with the PVDF powder to a concentration of 5% by weight. The polymer was dissolved in a solvent composed of 70% acetone and 30% DMF to a concentration of 50 g/L. The $TiO_2$ nano-particles were milled in a DMF solution which was then added to the mixed acetone/DMF solvent. The resulting solution was placed in an ultrasonic water bath at 30 °C for 3 h and then sonicated for one day. The thin films were finally prepared with a spin-coating process on a sheet glass which surface sputtering with a special metal coating.

### 2.2. Micro-structure pattern fabrication

A UV-LED (NCSU033A, wavelength 365 nm) was used to generate the UV rays. The optical power output was 190 mW. The irradiation source distance from the UV-LED to the surface of the PVDF/$TiO_2$ nano-composite film was set at 20 mm. The thickness of the PVDF/$TiO_2$ nano-composite film was 20 μm. The incident light distribution in the film is relative to the $TiO_2$ concentration and the film thickness [8], thicker films prevent the loss of incident light. UV-LED irradiation was performed at intervals in a dark room at 20 °C for 5 h. To fabricate grating patterns via UV irradiation, a mask made of a stainless steel sheet was set on the top of the PVDF/$TiO_2$ composite film, as shown in Fig. 1. The narrow periodic parallel slots in a $1 \times 1\,cm^2$ area of the stainless steel sheet were fabricated by semiconductor laser marking (DP-H50 L). The slots had a spacing of 1 mm and a width of 10 μm. The space between the mask and the film was 3 mm. A very small space was good for accurate replication of the pattern, but prevented additional heat loss. To promote the dissipation of heat generated by the irradiation source and increase the rate of PVDF degradation, deionised water was filled and discharged periodically into the gap between the mask and film.

### 2.3. Analysis of micro-structure patterns of film surface

A digital optical microscope (VH-8000) and SEM were used to study the morphology of the grating patterns on the PVDF/$TiO_2$ nano-composite film. A stylus profilometer (Ambios XP, American) was used to analyse profile parameters of the grating grooves. The change of chemical composition in the grooves was characterised using X-ray photoelectron spectroscopy (XPS).

## 3. Results and discussion

### 3.1. Morphology of structure

Fig. 2(a) shows the surface morphology of the PVDF/$TiO_2$ nano-composite films before UV irradiation. The white particles ranging in size from dozens to hundreds of nanometres are the $TiO_2$ nano-particles, and the figure shows that the $TiO_2$ particles were well dispersed within the polymer matrix. This effect of uniform distribution is closely associated with the degradation process. Fig. 2(b) shows a macroscopic optical photo of the period grating patterns applied to the surface of the PVDF/$TiO_2$ nano-composite film with the photocatalytic lithography. The insert at the top left of Fig. 2(b) shows the profile parameters of the grating grooves, which were obtained from continuous scanning of the stylus profilometer along the red line in Fig. 2(b). The groove spacing is 1 mm and the mean depth is approximately 4 μm. Fig. 2(c) shows a close-up macroscopic optical image of a groove with a width of 10 μm. The insert at the top left of Fig. 2(c) shows a close-up SEM image of the zone outside the groove which was under the stainless steel sheet, where it can be observed that there is no obvious morphological change.

Fig. 2(e) shows the close-up SEM image of a groove. Due to an uneven distribution of the slanted incident light through a slot, the edge of the side wall is a rounded corner. Near the groove edge, the $TiO_2$ nano-particles are homogeneously separated on the film surface. Near the groove centre with maximal light intensity, there are some globules with diameters that range from 500 nm to 1 μm. It was found that some cracks are formed at the edge of these globules. Fig. 2(d) shows a close-up image of these globules, where the $TiO_2$ particles are attached to the surface of the globules. This micrograph suggests that there is PVDF re-crystallisation occurring on the surface of the grooves [15]. The chains of PVDF curl and contract, thus forming the globules. The $TiO_2$ nano-particles follow the chains of the PVDF polymer and adhere to the surface of the re-crystallisation globules. The formation of cracks is due to stress concentrations at the edge of the globules. Fig. 2(f) shows a close-up SEM image of an area near the globules. The PVDF displays a severe etching in the form of lamellae. Cracks as large as dozens of nanometres were found at the interface of the lamellae.

### 3.2. XPS analysis

XPS was used to study the changes of the PVDF/$TiO_2$ nano-composite surface due to the UV irradiation. Fig. 3(a) shows the carbon signal in the XPS spectrum of the PVDF/$TiO_2$ nano-composite film. Three significant binding energy peaks are noted, where 286.1 eV and 290.5 eV correspond to the $CH_2$ and $CF_2$ bonds found in PVDF, respectively. Fig. 3(c) shows the carbon signal in the XPS spectrum of a groove zone, where there are 4 peaks shown. The peak of the binding energy at 288.1 eV corresponds to the CHF