J. Engg. and Appl. Sci. Vol. 35 No. 1 January - July 2016 *ISSN 1023-862X - eISSN 2518-4571*

PROJECTION ETCHING OF KERATIN THIN FILMS FOR FABRICATION OF SKIN STRUCTURE USING ARF EXCIMER LASER

Bibi Safia Haq[1,2], Hidayat Ullah Khan[3], Abdul Shakoor[4], Shahnaz Attaullah[5], Ishrat Rahim[1]

ABSTRACT

In this study the ablation efficiency and the phenomenology of the etched keratin patterns have been investigated and the surface modification was analysed. For effective studies of skin treatments, large areas of model skin need to be generated. Therefore an ArF excimer Laser wavelength (193nm) with the ability to pattern square mm areas per pulse was used even though the maximum repetition rates are typically an order of magnitude slower. Keratin samples with different film thicknesses were ablated with different pulses. The depth of the ablated keratin layers with different pulses were also measured by scanning the sample using a Dektak KLA-Tencor and the surface statistics of the ablated keratin sample have been analysed using a white light interferometer WYKO NT1100.

KEYWORDS: *ArF excimer Laser, ablation, keratin film, Skin structure, Bricks and mortar structure*

INTRODUCTION

Processing of biomaterials using laser technique is of great importance for micro fabrication, etching and cleaning of organic/inorganic materials[1]. Human skin is made up of keratinocytes. Therefore in stratum corneum keratin filaments is abundantly present. Stratum corneum is highly impermeable. To increase transdermal delivery, many chemical or physical methods have been considered for the disruption of stratum corneum microstructure[2-5]. Laser ablation of keratin films with various thicknesses has been analysed in the present study. To investigate skin structures based on lipid and keratin network, model skin structure has been fabricated in keratin film, using ArF excimer Laser. Skin, hair, nail and teeth contain keratin which is an extremely strong protein. To prepare samples from a solution, solid keratin can be extracted[6]. Skin is a sensory organ[7] and acts as a barrier to protect the body from serious health problems.

Stratum corneum is composed of[12-16] cell layers. It is a thin membrane and is compared to "bricks and mortar"[8] structure. In the epidermis, cells are arranged like a brick wall structure. Due to the degradation of the cells the outer most skin cells are continuously being replaced by new skin cells. During this renewal process keratinocytes at the bottom rise to the top and the old cells shed from the surface in the form of dead cells[9].

In the "brick and mortar" structure of skin, bricks are made of keratin while the gaps between these keratin bricks contain lipids and water behaving as mortar[10]. This protein/lipid polymer structure provides a barrier[11] as shown in Figure 1.

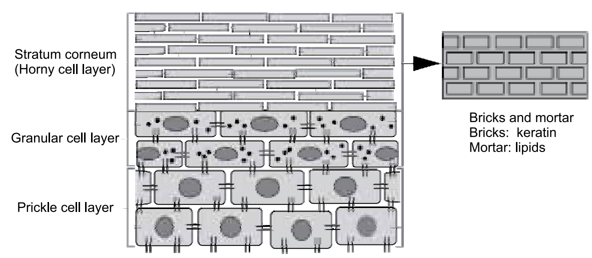

Figure 1. Schematic diagram of the structure of skin. The outer most layers are composed of Keratin based bricks with lipids as mortar[8].

Skin structure is weak in the absence of oil and moisture. It becomes dry, itchy and sometimes red, when water gets through the gapes. Use of emollient on skin surface fills the gaps between keratin bricks which keep it water tight and strong as shown in Figure 2 (a) and (b).

Figure 2. (a) Skin like brick wall without enough mortar (b) Brick wall is strong and water tight with mortar [12].

1 Department of Physics, JCW University of Peshawar, Khyber Pakhtunekhwa, Pakistan
2 Department of Physics and Mathematics, University of Hull, Hull, HU6 7RX, United Kingdom
3 Department of Physics University of Peshawar, Khyber Pakhtunekhwa, Pakistan
4 Department of Matrials, SAACME, Loughborugh University, LE11 3TU, United Kingdom
5 Department of Chemistry, JCW, University of Peshawar, Khyber Pakhtunekhwa, Pakistan

In another study keratin films of various thicknesses were ablated to investigate threshold energy and fluence for laser processing using a femtosecond laser system at 800 nm wavelength and also at 400nm wavelength using second harmonic generator of the laser source.

It was found that threshold fluence found for 400 nm wavelength ablation is less then laser ablation at 800 nm. Therefore for the fabrication of skin structure (brick and mortar), 400nm wavelength was used as shown in Figure 3. The threshold fluence at 400nm wavelength for thin film with thickness of 70nm was 30mJ/cm2 while it is 80mJ/cm2 for 250nm thick film[13].

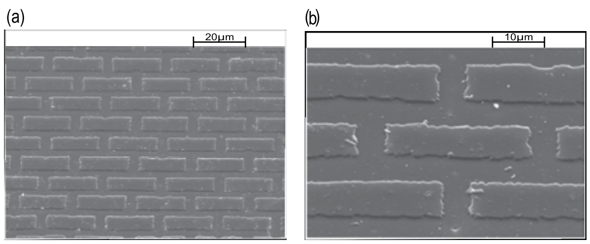

Figure 3. SEM structures for brick and mortar pattern in keratin film ablated at 400nm wavelength with 53nJ pulse energy. (a) shows bricks structures fabricated in thick film with thickness of 250nm and (b) shows bricks structures fabricated in thin film with thickness of 70nm[13].

As the femtosecond system requires pulses to overlap, the speed of the process depends on the spot size and laser repetition rate. The 10μm feature size (or smaller) specified for the model skin together with a maximum repetition rate of 1 kHz meant that for square centimetre areas, several hours would be required. For effective studies of skin treatments, large areas of model skin need to be generated. The use of an excimer laser with the ability to pattern square mm areas per pulse is therefore attractive even though the maximum repetition rates are typically an order of magnitude slower.

An excimer laser is a form of ultraviolet laser widely used in deep-ultraviolet photolithography[14] for the manufacturing of microelectronic devices, micromachining and eye surgery. The ultraviolet light emitted from the excimer laser can successfully remove surface layers without damaging and burning of the remaining material.

ArF and KrF are types of excimer laser and are widely used in high-resolution photolithography machines. The argon fluoride laser has a deep ultraviolet wavelength of 193 nm[15,16] and is used in the production of semiconductor integrated circuits, eye surgery, and micromachining.

MATERIAL AND STRUCTURE

Keratin present in epithelial tissue of skin contain intermediate filament (IF) made of Type I, Type II keratin and matrix proteins. Complex keratin structure shown in Figure 4, consists of cross linking with disulfide bonds[6]. To ablate keratin with laser beam, liquid form is generated to prepare keratin samples with required thicknesses from solid keratin extracted from various sources.

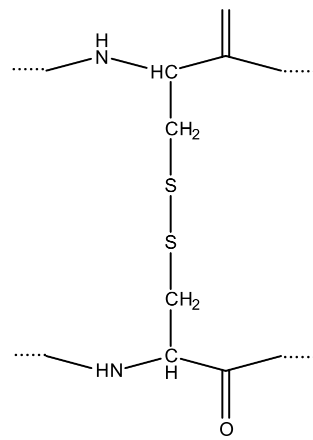

Figure 4. A scheme of cross linking due to cysteine in keratin

SAMPLE PREPARATION

In powder form keratin was obtained from TCI, Europe based on 85% quoted protein content. Liquid keratin was prepared from the extracted keratin powder. For sample preparation, a 250 μl mixed solution, based on 1 mg ml-[1] keratin protein and 2.5 wt% H_2O_2, was placed on a quartz plate of 25 × 25 mm^2. The sample was dried at 35oC for an hour in an oven. Stylus profilometer (DektakTX) was used to find the thickness of the sample and was found to be 70nm. In order to prepare samples for thick keratin films, liquid keratin of 150μl was poured on the substrate. Measurement shows approximately 250nm thickness.

Experimental arrangements

To ablate keratin film, the argon fluoride laser having short wavelength (193nm) was used. A reverse biased avalanche photodiode (FND 100Q with -90V bias) was used to measure the pulse duration. To avoid saturation light was back-scattered into the photodiode. A fast oscilloscope (HP Infiniium, 500MHz bandwidth, 2 GSa/s) was used to preserve the nanosecond rise time of the detector, and the coaxial cable from the FND100Q to the input was terminated into 50Ω. An excimer laser contains a mixture of halogen gas (fluorine or chlorine) and noble gas (argon, krypton, or xenon). A pulsed electrical discharge generates excited species that bond to form excited complexes (exciplexes). These states are unstable and decay rapidly (~nanoseconds) releasing the excess energy as an ultraviolet photon. As the ground state is dissociative, population inversion is maintained and high gains can be achieved. Although the UV wavelengths that can be generated by excimer lasers are becoming available from solid state systems, these gas lasers still uniquely offer large area, short pulse and beams that make them suitable for projection mask illumination. As an initial investigation a contact mask was placed

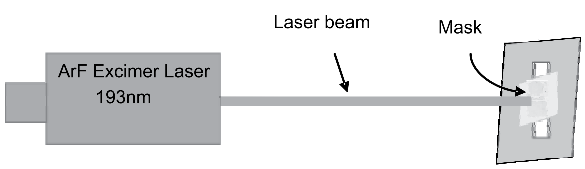

Figure 5. Schematic diagram showing Projection etching of keratin thin films using ArF excimer Laser. A contact mask placed on the keratin film on quartz substrate, was ablated with one, two and five pulses with 173mJ energy.

on the keratin film and the area flood illuminated with UV light from an ArF excimer laser Questek (Model 2860) shown in Figure 5.

RESULTS AND DISCUSSION

Amplitude mask

The argon fluoride laser was chosen as its short wavelength (193nm) and is strongly absorbed in the film. The relatively transparent quartz substrate has a much higher ablation threshold and so damage to the substrate is unlikely. Figure 6 shows ablation of keratin by the ArF

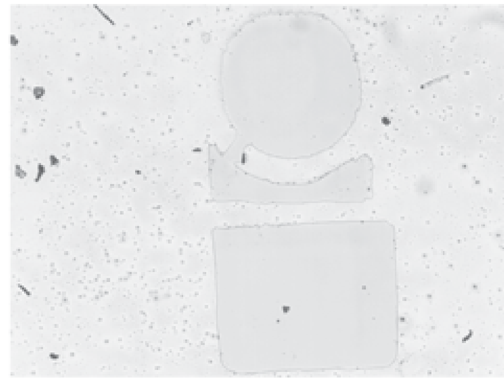

Figure 6. Keratin ablation by ArF Excimer laser at 193 nm wavelength using a contact mask. This image was obtained using an optical microscope.

laser using a simple contact mask. The sample, keratin film on quartz substrate, was ablated with one, two and five pulses with 173mJ energy.

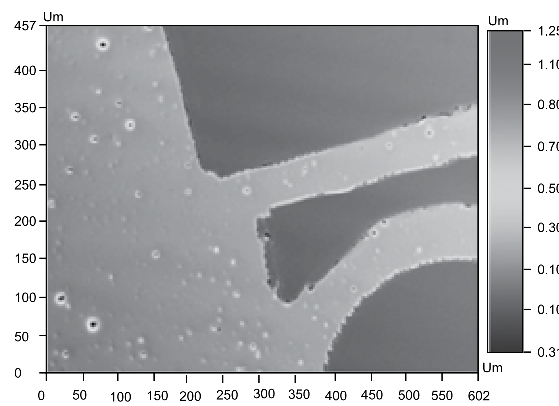

Figure 7. Surface data of the sample ablated by ArF Excimer laser at 193 nm wavelength using contact mask. The surface statistics of the ablated keratin sample have been analysed using a white light interferometer WYKO NT1100.

The sample ablated at 193 nm wavelength was also analysed with the help of a white light interferometer WYKO NT1100. Surface data of the analysed sample is shown in Figure 7.

The depth of the ablated keratin layers with different pulses were measured by scanning the sample using a Dektak KLA-Tencor. Figure 8 show ablation scan of the keratin sample. The sample was ablated with five

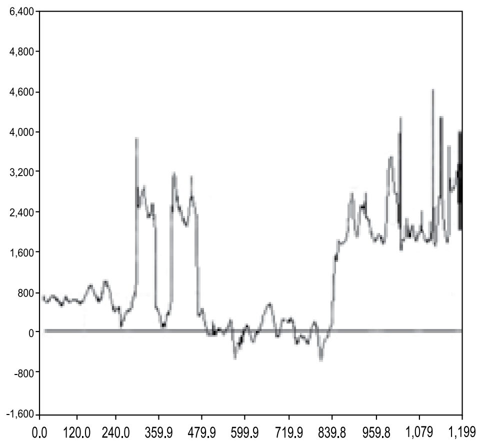

Figure 8. Scan of ablated areas on Keratin thick film irradiated with 5 pulses of Excimer ArF 193nm wavelength laser. The depth of the ablated layer is approximately 240nm.

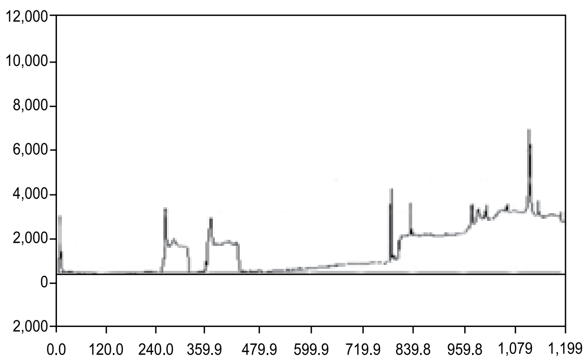

Figure 9. Scan of ablated areas on Keratin thick film irradiated with 2 pulses of Excimer ArF 193nm wavelength laser. The depth of the ablated layer is approximately 190nm.

pulses and the depth of the sample was found to be approximately 240 nm.

The scan of the keratin sample ablated with 2 pulses is shown in Figure 9. The depth of the ablated layer was

Keratin samples with different film thicknesses were ablated with single pulse. The depth of the thick film with single pulse was found to be approximately 170 nm as shown in Figure 10 while the thin film ablation depth was found as 77nm shown in Figure 11.

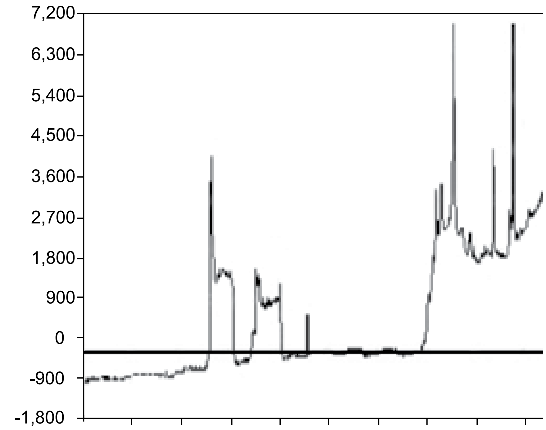

Figure 10. Scan of ablated areas on Keratin thick film irradiated with 1 pulse from the ArF 193nm wavelength laser. The depth of the ablated layer is approximately 170nm.

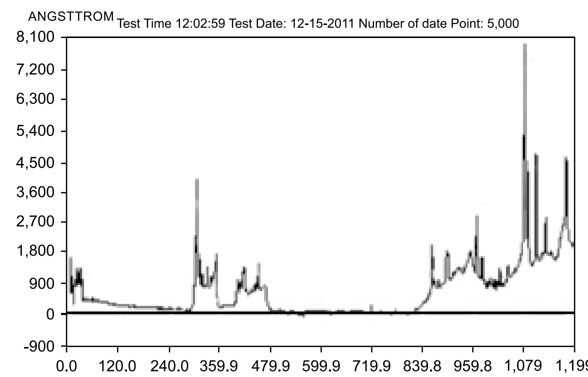

Figure 11. Scan of ablated area at the edge of the Keratin film irradiated with 1 pulse from the ArF laser. The depth of the ablated layer is approximately 77nm.

PHASE MASK

Keratin patterning at micron or sub-micron length scales may be an ultimate requirement. Due to the fibrous nature of keratin, material itself may not support such small features. Therefore, interference fringes were used to generate a pattern that explore limit to the resolution. Keratin film was illuminated with the 193nm laser light along with a phase mask placed close to the film. Figure 12 (b) shows surface of the keratin film after irradiation. Approximately 1μm feature sizes fabricated in the keratin material is indicated in the SEM image.

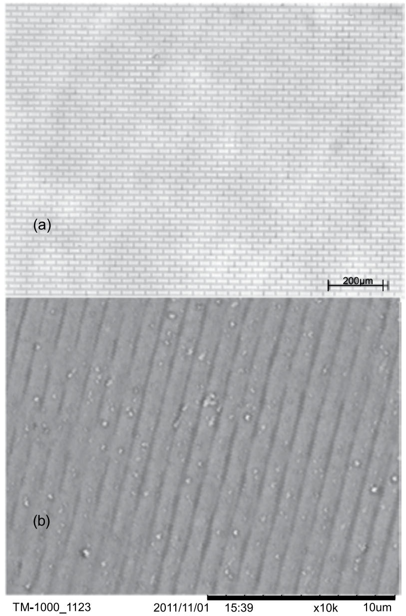

Figure 12. (a) Bricks and mortar structure fabricated in keratin film using femtosecond laser analysed by optical microscope. (b) SEM image of Keratin ablation using an ArF laser at 193 nm wavelength to illuminate a quartz phase mask placed in contact with the film[13].

CONCLUSION

In the present study an ArF excimer laser operating at 193 nm wavelength was used to fabricate pattern in keratin films. The ablation efficiency and the phenomenology of the etched keratin patterns have been investigated and the surface modification was analysed. The surface morphology of ablated areas was analyzed by means of optical microscopy and scanning electron microscope. The sample ablated at 193 nm wavelength was also analysed with the help of a white light interferometer WYKO NT1100. This has application in forming model skin surfaces to allow the study of the effect of applying creams to human skin.

Thus we can conclude that ArF laser light can be used to prepare keratin based wall structure as a model surface for skin care products. As keratin has very low ablation threshold, therefore femtosecond laser systems are practical for laser processing. However, for industrial trial, excimer laser are likely to be used, where larger areas can be processed.

REFERENCES

1. *Tsuboi, Y., Kimoto, N., Kabeshita, M. and Itaya, A., 2001. "Pulsed laser deposition of collagen and keratin". Journal of Photochemistry and Photobiology A: Chemistry 145: 209–214.*

2. *Jung-Hwan P., Jeong-Woo L., Yeu-Chun K. and Prausnitz, M. R., 2008. "The effect of heat on skin permeability". International Journal of Pharmaceutics 359: 94–103.*

3. *Cross, S. E. and Roberts, M. S., 2004. "Physical enhancement of transdermal drug application: is delivery technology keeping up with phamaceutical development?". Curr. Drug Deliv. 1: 81–92.*

4. *Down, J. and Harvey, N. G., 2003. "Minimally invasive systems for transdermal drug delivery". In: Guy, R. H. and Hadgraft, J., eds., Marcel Dekker, New York.*

5. *Schuetz, Y. B., Naik, A., Guy, R. H. and Y. N. Kalia, 2005. "Emerging strategies for the transdermal delivery of peptide and protein drugs". Exp. Opin. Drug Deliv. 2: 533–548.*

6. *Nakamura, A., Arimoto, M., Takeuchi, K. and Fujii, T., 2002. "A Rapid Extraction Procedure of Human Hair Proteins and Identification of Phosphorylated Species". Biol. Pharm. Bull. 25: 569—572.*

7. *Richardson, M., 2003. "Understanding the structure and function of the skin." Nursing Times.net 99: 46-48.*

8. *Imae, T., 2014. Skin Bioscience: A Molecular Approach: CRC Press.*

9. *Bensouilah, J. and Buck, P., 2006. "Skin structure and function". Aromadermatology:Aromatherapy in the Treatment and Care of Common Skin Conditions. Abingdon: Radcliffe Publishing, 264.*

10. *6/3/2012."Understanding the causes of skin disease," www.hse.gov.uk,*

11. *Nemes, Z. and Steinert, P.M., 1999. "Bricks and*

mortar of the epidermal barrier". Experimental and molecular medicine 31: 5-19.

12. *23/3/2012, "What is going on with my skin? Damaged skin barrier". www.eczemazones.co.uk,.*
13. *Haq, B., Khan, H., Dou, Y., Alam, K., Attaullah, S. and Zari, I., 2015. "Keratin film ablation for the fabrication of brick and mortar skin structure using femtosecond laser pulses". Applied Physics A 120: 1415-1425.*
14. *Jain, K., Willson, C. G. and Lin, B. J., 1982. "Ultrafast Deep UV Lithography with Excimer Lasers". IEEE Electron Device Letters EDL-3: 53-55.*
15. *Basting, D. and Marowsky, G., 2005. Excimer Laser Technology: Springer. IEEE Elcetron Device Letters EDL-3. 53-55.*
16. *Basting, D. and Morowsky, G., 2005. Excimer Laser Technology: Springer.*