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SECM imaging of latent fingerprints developed by deposition of Al-doped ZnO thin film

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ABSTRACT

A novel vacuum metal deposition (VMD) based technique has been efficiently employed for the visualization of latent fingerprints on glass and plastic substrates. Al-doped ZnO thin film (ZAO) was deposited on the bare surface and the valleys between the fingerprint ridges by direct current magnetron sputtering with the oblique target, which yielded normal development of latent fingerprints. The enhanced results of latent fingerprints have been photographed with good contrast by a conventional digital camera. Additionally, an electrochemical method, scanning electrochemical microscopy (SECM), has also been successfully applied to the image acquisition of a latent fingerprint developed on the glass surface due to its superb sensitivity toward the small variation of the conductivities at the substrate surface. The SECM image of a latent fingerprint on glass substrate provided good contrast between valleys and ridges and micrometer-scale resolution images of fingerprints under wet conditions by using ferrocene methanol as a redox mediator to detect the topology of the fingerprint deposits in constant-height feedback mode.

1. Introduction

From fingertips to wrist, the palm of a hand is covered by minute ridges of skin, called papillary or friction ridges, with the depressions between the ridges termed valleys. Indeed, every fingertip has a unique and distinctive ridge pattern [1] and fingerprint is an important form of physical evidence for the identification of individuals [2], such as forensic investigation [3,4], law enforcement [5], access control [6], or medical diagnostics [7]. A fingerprint, an impression of the ridge pattern, is formed on a surface when a finger touches the surface, and it is usually invisible in daylight to the naked eye. These invisible or latent fingerprints, which are produced just by perspiration and other natural secretions on the skin surface (ranging from ordinary sweat to a sebum-rich deposit), are rarely clear enough to photograph directly and some means of "development" is required to enhance visualization of the ridge pattern. Various elegant physical (powdering, small particle reagent, vacuum metal deposition), chemical (iodine, cyanoacrylate, ninhydrin and its analogs), optical (laser, fluorescence, UV/vis and infrared absorption), and combination techniques have been explored for the visualization or enhancement of latent fingerprints under specific circumstances [8–14]. Recently, there has been a renewal of fundamental interest in detecting quantities of drugs, explosive residues, and other exogenous substances in fingerprints [15–18]. Meanwhile, investigators may detect the metabolites of who left the fingerprint from a single latent fingerprint and get more information. In spite of a great variety of existing fingerprint techniques, there are no method(s) adequate for all surfaces/circumstances and a significant number of fingerprints remain undetectable. Therefore, researchers continue aiming at developing new, more versatile methods, or trying to improve the existing techniques.

Surfaces like glass and plastics are classified as smooth, nonporous surfaces with relatively high fingerprint residue retaining capacity [19] and they are among the most common substrates on which suspected latent fingerprints are searched. A large number of methods have been reported in the literature for the fingerprint development on these substrates and vacuum metal deposition (VMD) is the conventionally and commonly used method [20]. The VMD has been proven to be a sensitive technique, since it has been reported to develop latent fingerprints on plastic surfaces in the 1970s [21]. Generally, this technique consists of the evaporation and deposition of gold and then zinc under high vacuum, and the zinc will deposit uniformly across the whole surface except where fingerprint residues are present. A previously identified difficulty with this method is that excess gold deposition prevents effective

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zinc deposition and so inhibits latent fingerprint development [22]. Therefore, development of a latent fingerprint by VMD using a single metal, or one step rather than two steps used previously is a prosperous orientation in the future. Very recently, thermal evaporation of ZnO was conducted to develop a latent fingerprint on plastic surfaces without using Au clusters as the seed layer [23]. However, the ZnO thin film has relatively poor conductivity. Our objective is to develop a simplified vacuum deposition method with multifunctional Al-doped ZnO thin film (ZAO) which cannot only enhance the visualization of the latent fingerprint, but also benefit to achieve their image by electrochemical techniques.

Scanning electrochemical microscopy (SECM) is a scanning probe technique as well as a powerful electrochemical technique and has been applied extensively during the past three decades [24–29]. SECM is a versatile technique for extracting electron-transfer kinetics information [30,31], for high-resolution imaging of the chemical activity or topography of various interfaces on a localized scale [32], for micropatterning [33] and studying biological systems [34]. SECM can be employed to obtain chemical reactivity images of surfaces and is able to resolve differences on the micron or sub-micron length scale. It has been used in the feedback mode to image silver or copper stained proteins by generating an oxidizer at the microelectrode to oxidize these metals [35]. Moreover, previous reports showed that SECM combined with silver staining could be applied to image protein-modified fingerprints on a porous poly membrane and real latent fingerprints on glass surface enhanced by multi-metal-deposition [36]. Compared with the commonly used optical imaging fingerprint technique, SECM imaging can avoid the interference of the substrate background-color. Meanwhile, this methodology takes a significant advantage of the high sensitivity of SECM toward the small variation of the conductivity at the substrate surface for ultrasensitive imaging of the latent fingerprints.

In this work, we have developed a novel strategy to improve the existing VMD technique for the visualization of latent fingerprints on glass and plastic substrates by depositing multifunctional ZAO thin films and then achieve their images by both the conventional photographic and creative electrochemical techniques. The ZAO thin films were directly coated onto non-metallic materials by direct current magnetron sputtering with the oblique target for the development of latent fingerprint without using Au clusters as the seed layer. Thereafter, SECM has been successfully applied to the image acquisition of the developed fingerprint on glass substrate due to the relative good conductivity of ZAO thin film.

2. Experimental

2.1. Reagents

All chemicals were used as received [ferrocene methanol (FcMeOH, Alfa Aesar), potassium nitrate (KNO_3, >99%, Fluka)]. Water was deionized to a conductivity of 18.2 $\mu S\,cm^{-1}$ using a Milli Q plus 185 from Millipore. Alumina 1 μm (0.3 and 0.05 μm,) and Mastertex polishing cloths from Buehler were employed to polish the 25-μm-diameter microelectrode.

2.2. Fingerprints sample

An optical microscopic glass sheet and polyethylene terephthalate (PET) sheet were cut into squares of 15 mm × 15 mm. The glass and PET substrates were ultrasonically rinsed in acetone, ethanol, and deionized water, followed by drying in the air and then used to study development of latent fingerprints. Prior to the fingerprint deposition, the donor's hands were thoroughly washed with soap, rinsed with water, and dried. Sebaceous fingerprints (sebum-rich) were obtained from the donor by gently rubbing his fingertip over forehead and then pressing it on the glass and PET sheets with a minimal pressure. Fresh fingerprints were kept airtight for 1 h before being positioned in the VMD system.

2.3. Magnetron sputtering system

The DC magnetron sputtering system used (KYKY Technology Development Ltd.) has the target inclined to the substrate at an angle of about 45° and has been described elsewhere in detail [37]. ZAO films with a thickness of 250 nm were sputter-deposited on the glass and plastic substrates with fingerprints at 300 K using a sintered ceramic ZnO + 2 wt% Al_2O_3 target (99.99% in purity) of 50 mm in diameter. During the sputter-deposition, an Ar gas (99.9995% in purity) pressure was adjusted to 0.4 Pa. A distance between the target and the substrate was about 100 mm. The sputtering power applied to the target was fixed at 150 W. The deposition rate was 10 $nm\,min^{-1}$. The deposition time was 25 min. Prior to deposition, the working chamber was evacuated to a pressure lower than 2×10^{-4} Pa using a turbo molecular pump. The substrate holder was rotated using a stepping motor during deposition in order to obtain a uniformly thick film.

2.4. Photograph and SEM characterization

The fingerprints developed by ZAO deposition were visually checked and their photographs were taken under an optical microscope (World Precision Instruments, PZMTIV). A piece of black paper was placed underneath the specimens to facilitate fingerprint inspection. The same sample was also further characterized by SEM (JEOL, JSE-6510A).

2.5. Electrochemical apparatus

The ZAO enhanced fingerprints on transparent glass were then electrochemically imaged by SECM (CH Instruments Model CHI 920C, USA). A three-electrode setup was employed with a 25-μm-diameter Pt microelectrode as the amperometric SECM probe. The counter and quasi-reference (QRE) electrodes were a Pt wire and a silver wire, respectively. The fingerprint sample was placed in the SECM Teflon cell and then this cell assembly was secured onto a platform which includes three screws for leveling the substrate surface manually. The Pt microelectrode was prepared from a 25-μm-diameter Pt wire using the procedures described previously [38]. The RG (ratio of the outer glass diameter to the diameter of the wire) value of the microelectrode was about 5. Before the SECM imaging experiment, the microelectrode was polished using polishing cloths and solutions of alumina, washed with acetone, ethanol, and deionized water, then dried in the air prior to each measurement. An optical microscope (Olympus X-51, Japan) was used to first check the quality of the prepared probe. To further check the electrochemical behavior of the probe, the cyclic voltammogram measurements were performed with a solution of ferrocene methanol (2×10^{-3} mol l^{-1} in 0.1 mol l^{-1} KNO_3 in H_2O). SECM feedback images of fingerprints were performed at a probe potential of E_{probe} = 0.3 V vs Ag QRE while the sample was at open circuit potential (OCP). Although this SECM instrument is in principle capable of scanning an area of 5 cm × 5 cm, with the aim of illustration, an image of smaller area (e.g., 0.4 cm × 0.15 cm) was shown here. All of the SECM experiments were carried out at room temperature and the SECM image data was treated by using FemtoScan software.

3. Results and discussion

Optical microscope images of fresh and developed latent fingerprints by ZAO deposition on the glass and plastic substrate