ALL PRINTED BISTABLE REFLECTIVE DISPLAYS: PRINTABLE ELECTROPHORETIC INK and ALL PRINTED METAL-INSULATOR-METAL DIODES

By

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Submitted to the Department of Materials Science and Engineering
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ABSTRACT

We have printed Metal-Insulator-Metal Diodes onto flexible substrates using hybrid polymer and metal-metal oxide inks. Successful device structures were printed by means of several processes including 1] a two step process of Ta in polymer matrix with thermally grown oxide followed by printed Cr in polymer and 2] a one step process of pre-oxidized Ta microparticles in polymer. Back-to-back diode I-V characteristics were demonstrated with tunable turn-on voltages between 5V and 100V. Coupled with a fully printable bistable, electronically addressable electrophoretic ink which we have developed, such systems open the way for all printed, reflective, bistable electronic displays.

Thesis Supervisor: Joseph M. Jacobson
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1. INTRODUCTION

Metal-Insulator-Metal diodes as the switching mechanisms in active matrix displays are getting increasing attention. Since the first proposal of the utilization of the active switching element in matrix displays[1], many different technologies have been introduced. At present, almost all active matrix LCDs use thin film transistors (TFTs) made with either amorphous silicon or poly-silicon. TFTs require high processing temperatures, complicated integrated circuit-type fabrication processes, which therefore raises the cost of production. First introduced as an active element material by Baraff in 1981 [2], MIM diodes offer some attractive advantages. MIM diodes are simple to fabricate and use low-cost substrates and equipment. The symmetric I-V characteristic is also very important. However, commercial MIM fabrication processes, although relatively simple, still require vacuum deposition of metals as well as photolithographic steps. Therefore, the manufacturing cost is still high. Moreover, MIM diode production yields are low due to extremely low tolerance to pinhole defects.

In this paper we show that MIM diodes can be fabricated by simple conventional methods such as screen printing onto a suitable substrate at room temperature. Using very fine metal powder with a suitable polymer binder, we have printed working devices with processing temperatures under 110 °C (the curing temperature of the polymer). The low yield problem due to pinhole defects is altogether avoided because no atomic metalization, such as sputtering, is employed, and because Ta/TaOx is embedded within a polymer matrix. Utilizing the non-linearity of these devices, all-printed, active matrix electrophoretic display pixels using electronic-ink have been successfully fabricated.

2. EXPERIMENTAL PROCEDURE

2.1 FABRICATION OF MIM DIODE

A MIM diode sandwich structure is usually made up of metal-insulator-metal thin films. Typically tantalum is used as the base metal with an anodically grown oxide. Alternatively, silicon nitride can be deposited on top of the tantalum to form the insulating layer. Chromium and tantalum have been used as the top metal layer.

In this paper, three sets of experimental devices were created. The first set of experimental device structures were MIM diodes fabricated with Ta foil as the base metal, anodically grown Ta oxide as the insulating layer, and Cr powder in polymer binder as the top metal. The second set of devices were MIM diodes using Ta powder in polymer binder as the base metal, anodically grown Ta oxide as the insulating layer, and Cr in polymer binder as the top metal layer. Finally, a third set of devices were constructed by depositing a layer of thermally pre-oxidized Ta powder in a polymer binder directly onto a substrate. The thermal pre-oxidation step was used to form a thin oxide layer on the Ta powder particles. By using pre-oxidized powder, the post-deposition oxidation step was eliminated, enabling faster and more efficient fabrication processes.

2.1.1 Tantalum Foil Experiments

Tantalum foil (99.995%, Alfa Æsar) was cleaned to remove any organic surface contaminations, but the native oxide layer was not removed, for HF dip would have been necessary. The Ta foil was then cut to dimensions of 10mm x 10mm x 0.127mm, and was anodized in 0.1M citric acid aqueous solution to grow an oxide layer. The cathode was made of Ta matal, to minimize the impurity in the oxide formed. The thickness of the oxide is controlled by

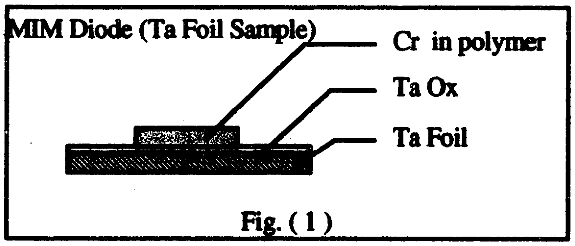

Fig. (1)

the final value of the anodization voltage [3], and typically 100V was used. Chromium powder (99.5%, < 5 µm) was mixed with polymer binder (Acheson Colloids Company, Electrodag 23DD146A) and printed on top of the oxide layer. The samples were then heated in a convection furnace at 110°C for 20 minutes allowing the polymer binder to cure and form a conductive Cr layer. Figure 1 shows the simple MIM configuration produced by this fabrication process.

2.1.2 Tantalum Powder Experiments (post anodic oxidation)

Tantalum metal powder (99.9%, < 2 µm, Alfa Æsar) was mixed with polymer binder (Acheson Colloids Company, Electrodag 23DD146A) and printed on top of a copper electrode and was then cured in a convection oven at 110 °C for 20 minutes. Following this curing schedule, the sample was anodically oxidized in 0.1M citric acid. The exposed copper electrode was covered with epoxy to avoid preferential oxidation of the copper. Cr powder in polymer binder (Acheson Colloids Company, Electrodag 23DD146A) was then printed on top of the oxide and cured at 110 °C for 20 minutes to complete the structure as illustrated in figure 2.

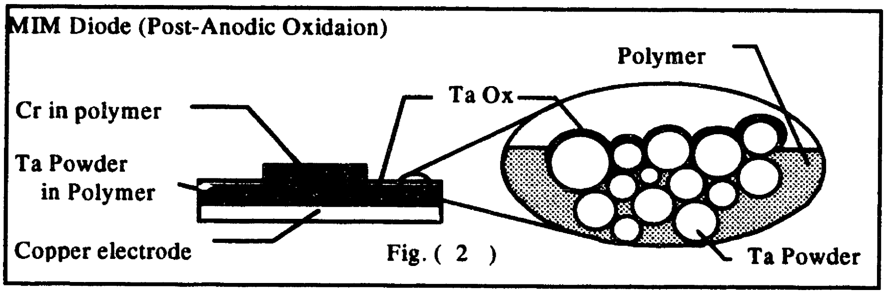

Fig. (2)

2.1.3 Tantalum Powder Experiments (pre-thermal oxidation)

Two methods were used to produce oxide-coated tantalum powders: heat at 300°C with water or heat at 250°C and increase to 300°C.

Tantalum powder (99.9%, < 2 µm, Alfa Æsar) was added to a ceramic crucible. The tantalum powder was then hydrated with just enough distilled water to wet all the powders. The crucible was then placed in a furnace heated to 300°C, filled with air.

Often at 300°C, the whole powder batch underwent a violent oxidation and entire batch turned to a white oxide. For an unknown reason, the addition of water seemed to help prevent this complete, uncontrolled oxidation of the powder. The addition of the water may induce the rapid formation of a thin oxide layer on the surface of the metal powder. This layer would act as an oxygen diffusion barrier, thus protecting the metal inside. The powder was heated for 4 hours to achieve 80V turn-on voltage.

At 250°C, the previously observed uncontrolled oxidation does not occurs. Ta samples were heated in the absence of water at 250°C until the formation of a thin oxide layer was observed. This typically takes 20 hours. The furnace temperature was then raised to 300°C and held for desired amount of time, typically 4 hours to achieve turn-on voltage of 80V. The crucible was removed at the end of this time and air-cooled at room temperature.

After oxidizing by either method, the resulting product was a light brown powder consisting of oxide-coated tantalum particles. This powder was then mixed with a vinyl resin solution (Acheson Electrodag 23DD146A polymer) and was printed by either conventional screen printing, or by use of a doctor blade to form a thin-film on the top of a copper electrode mounted on a glass or a mylar sheet. The resulting structure was then cured in a convection oven at 110°C for 20 minutes. A mixture of chromium powder and polymer(Acheson Electrodag 23DD146A) was printed on the Ta/TaOx and cured in the same way. The resulting product was a metal-insulator-metal structure, as illustrated in figure 3.

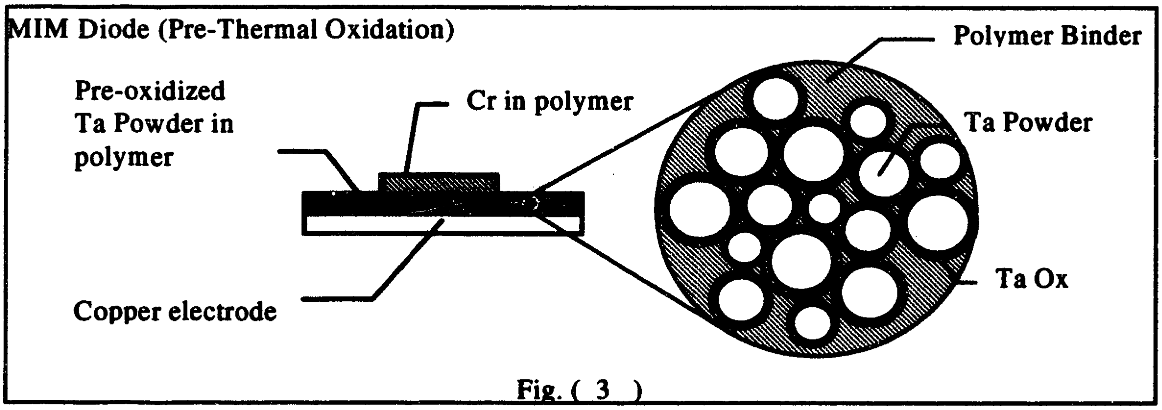

Fig. (3)

3. RESULTS AND DISCUSSION

3.1 ALL-PRINTED MIM DIODES

The MIM film exhibits a symmetrical back-to-back diode current-voltage characteristic. For all MIM films, depending on preparation, the diode turn-on voltage could be tuned between 2V and 100V by adjusting oxide thickness. Figure 4 shows a typical I-V curve of a Ta foil sample. Threshold voltages between 2 and 10 volts were obtained by altering the Ta oxide thickness. These low threshold voltages are likely to be due to local regions of thinner oxide caused by surface impurities and poor native oxides. One such region is shown in the E-SEM micrograph presented in figure 5. This lack of uniformity in oxide thickness also resulted in a low on/off ratio (at V and V/2) on the order of 10.

The second set of experimental MIM structures were formed by post-anodic oxidation of the tantalum powder-in-binder film. The anodic oxidation procedure produces an amorphous oxide coating with uniform thickness. The rate limiting step during anodization is the diffusion of oxygen through the oxide-metal interface [5]. The thickness of the anodized layer follows a square root dependence on time for very long times. This may indicate that diffusion is the rate-limiting step [6]. The reason that uniform layers are grown is that if there is a spot on the film which happens to grow thicker than the surrounding material, the diffusion in this region will slow due to the increase in length of the diffusion path. Superior uniformity of oxide thickness is reflected in the higher on/off ratios on the order of 10^2. An I-V curve is presented in figure 6. It is also observed that an increase in oxide thickness causes an increase in the threshold voltage, as expected. We expect to increase the on/off ratio with cleaner, oxide-free starting powder, and an optimized anodization schedule to create more uniform, high quality oxide layers. However, a HF dip will be required to strip the native oxide from the tantalum. This action will undoubtedly destroy the pre-formed device structure. It is also difficult to anodize the free powders because the anode can't be directly attached to the powder. Therefore, the thermal pre-oxidation of the powder was chosen as the most suitable method for MIM construction.

The third set of experimental MIM structures used thermally pre-oxidized Ta powders. The Ta powder turned entirely to oxide in very short times at temperatures greater than 400 °C. This is due to the tantalum oxide becoming crystalline and tending to spall, leaving the metal unprotected [7]. Successful devices were made from powders that were oxidized at temperatures lower then 300°C. At these lower temperatures, oxides are amorphous and adhere well to the metal, forming a protective coating [8]. The TEM micrograph in figure 8 shows the clear boundary between the oxide and metal regions. The oxide thickness in this particular photo is about 3nm, and electron diffraction revealed that it is amorphous, as expected. The electrical characteristics of the devices fabricated using pre-oxidized powders have been proven to be superior. This is likely to be due to the more complete coverage of the oxide. The TEM micrograph in figure 8 shows a fairly uniform, defect free oxide layer. The on/off ratio at V and V/2 is on the order of 10^3. As shown in figure 7, the devices have virtually zero leakage current.

3.2 ALL-PRINTED ELECTROPHORETIC DISPLAY

3.2.1 Electronic ink

To demonstrate the non-linearity of the MIM diode and it's role as an active matrix element, a simple display structure was constructed using electronic ink (e-ink) as the display material. Electronically addressable ink which consists of a microencapsulated electophoretic display suspension was previously developed in the MIT Media Laboratory [4]. Each 30 μm microcapsule is filled with either permanently charged nanoparticles in a dyed dielectric fluid, or two opposite charged particles of contrasting colors in organic solvent. In either case the liquid medium is density-matched to the particles. When an electric field is applied to the e-ink, depending on the polarity, the charged particles move up or down, changing the color of the display. The system is completely bistable. Electronic ink was obtained from E-Ink Corporation (Cambridge, MA).

3.2.2 The first all-printed electrophoretic display

Electronic ink was printed onto a sheet of ITO-coated mylar. Conductive silver ink (Acheson Colloidal Company, Electrodag 479SS) was printed on top of the e-ink. Finally, a pre-thermally oxidized Ta powder-in-polymer and Cr-in-polymer MIM structure was printed as the top layer in the display device. The first successful all printed active matrix display used four pixels. Two e-ink pixels contained the MIM film, and two pixels did not. The two pixels without the MIM film exhibited switching behavior at voltage levels of V and V/2. This result illustrates the need for a non-linear element to overcome the half-voltage select problem frequently encountered with matrix addressing schemes. The two remaining e-ink pixels with a MIM film were also subjected to voltage levels of V and V/2. The pixel subjected to V exhibited switching behavior. The V/2 pixel did not. This result demonstrates that a MIM film can indeed be used as the active matrix element to effectively overcome the half-select problem, as illustrated in the figure 9.

4. CONCLUSIONS

The first all-printed metal-insulator-metal active matrix element fabricated at low processing temperatures for display applications has been demonstrated. Extremely non-linear printed MIM diodes have successfully switched pixels without the half-voltage select problem. In the fabrication of printed MIM diode films, pre-oxidation of the powder simplifies the processing a great deal. We have selected the thermal oxidation of the powder as the preferred oxidation process. Thermal pre-oxidation of the powders has several advantages. First, the powders are easy to produce at a very low cost. Second, it is easy to control the thickness of the oxide, which ultimately leads to control of the threshold voltage. Third, it is easy to produce large batches of material at a time. Fourth, because no further oxidation step of any kind is required, many restrictions on the overall process are eliminated. Finally, since each oxide-coated Ta particle is non-conductive, it is not necessary to pattern the Ta/TaOx layer, which facilitates the production of large area displays. It is necessary only to pattern the ITO and the Cr electrodes, which can be done quite easily. With further improvements in M IM non-linearity, we propose that a large all-printed active matrix display using MIM diode films can be fabricated at very low cost.

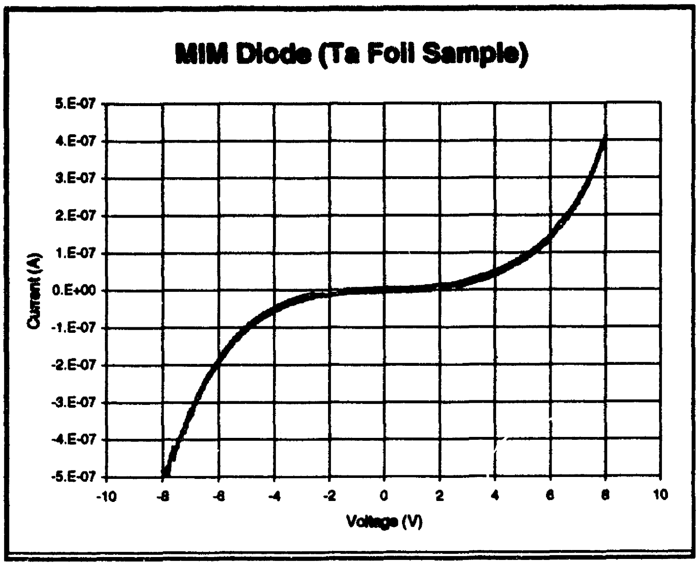

Fig. (4) Ta foil MIM diode showing its symmetric back-to-back diode I-V characteristic.

Fig. (5) E-SEM micrograph of the surface of the Ta foil after anodic oxidation. Note the pinhole defects and thinner spots which lead to low on/off ratio.

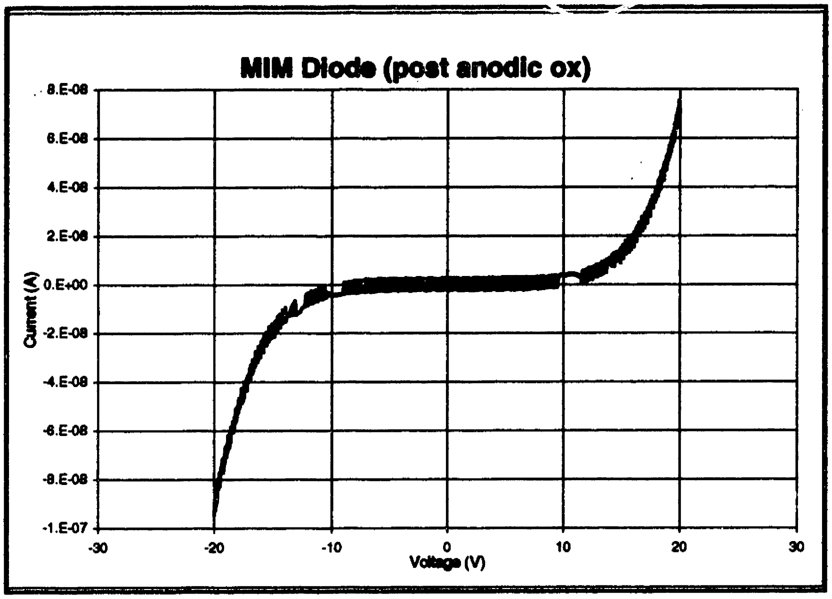

Fig. (6) MIM diode fabricated by post anodic oxidation showing good symmetry and on/off ratio.

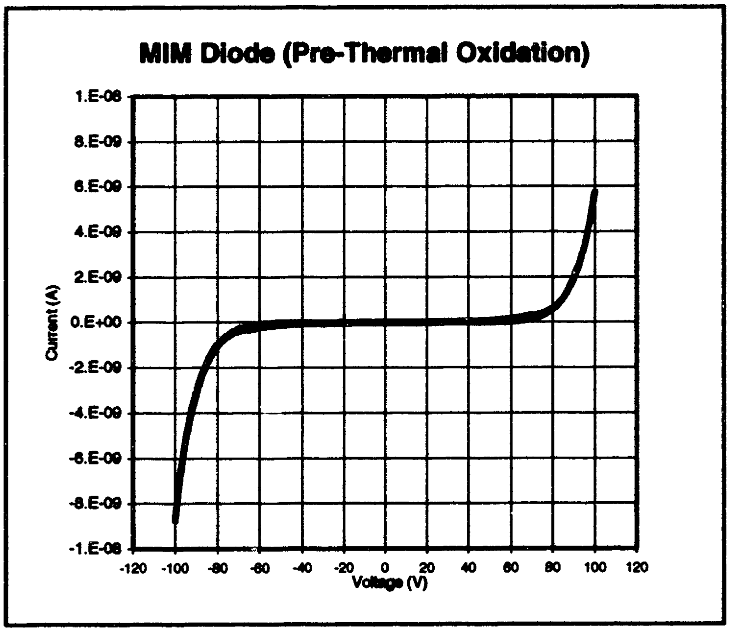

Fig. (7) I-V curve of a MIM diode made with pre-thermally oxidized Ta powder, with good symmetry and very high on/off ratio with extremely low leakage current.

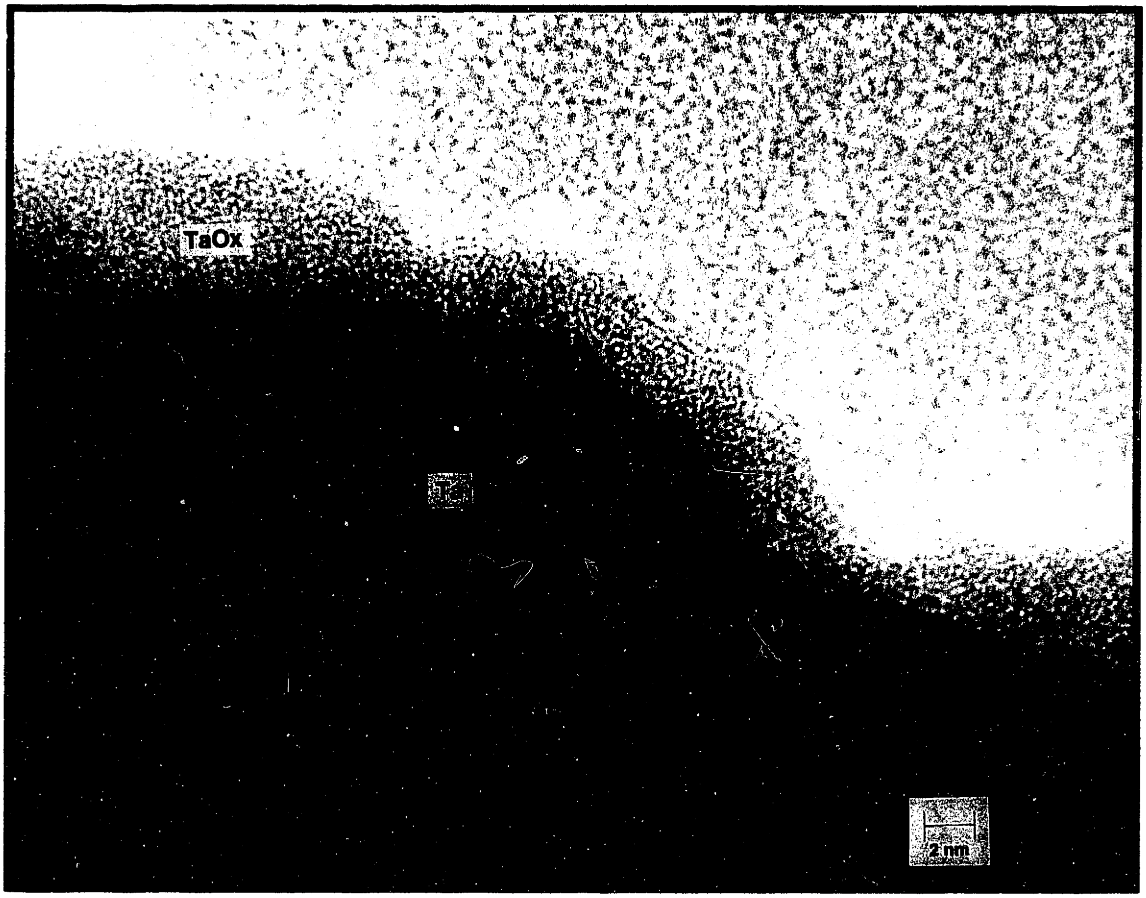

Fig. (8) TEM micrograph of the fractured section of pre-thermally oxidized powder, depicting clear Ta/TaOx boundary and amorphous oxide layer of 3 - 4 nm thickness.

Demonstration of All-Printed Display Pixels Without Half-Voltage Select Problem

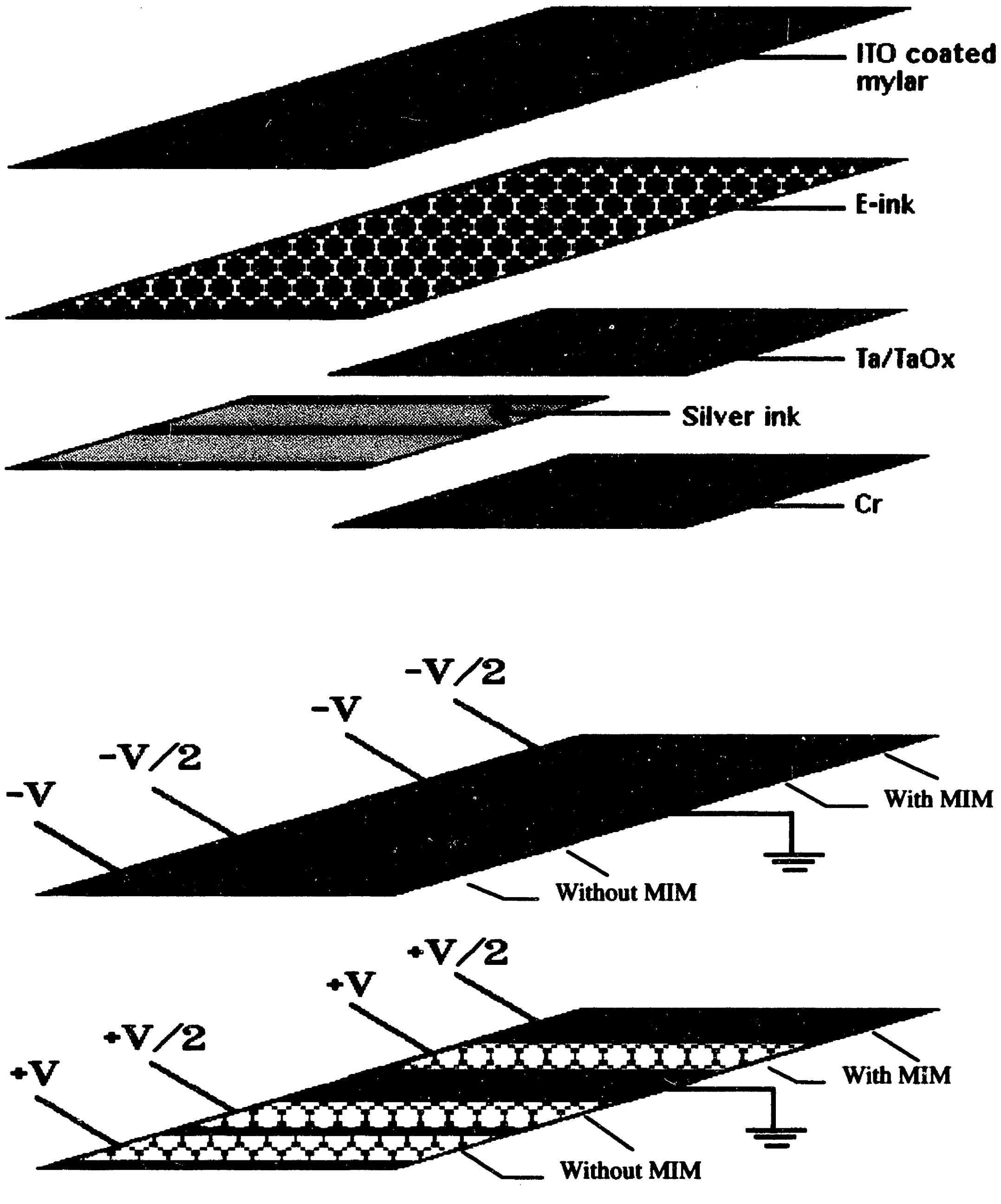

Fig. (9) Construction of the all-printed electrophoretic display pixels using MIM diodes, and the demonstration of elimination of the half-voltage select problem.

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BIOGRAPHICAL DATA

Jaeyong Park was born on April 3, 1975 in Seoul, Korea. He moved to the United States in October 1987 and lived in Forest Hills, New York before attending MIT in 1994. He received a S.B. in Materials Science and Engineering in June, 1998, and is presently studying Materials Science and Engineering at Stanford University graduate school.

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