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Exploiting voltage contrast scanning electron microscopy to investigate conductive polymer composite resettable fuse devices

A. P. Burden[a,*], W. Guo[b] and J. L. Hutchison[a]
[a]*Department of Materials, University of Oxford, Parks Road, Oxford OX1 3PH, U.K.*
[b]*Corporate Technology Europe, Raychem Ltd., Faraday Road, Swindon SN3 5HH, U.K.*
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Voltage contrast scanning electron microscopy has been exploited to investigate the operating stability of conductive polymer composite resettable fuse devices. It has been shown that the technique enables the active region of the device to be imaged and, hence, its position and shape to be compared after a succession of operating cycles and as a consequence of the position of the attached surface electrodes. This leads to a useful diagnostic tool for the investigation of the configuration of such devices and the morphology of the conductive polymer composite material of which they are made. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

A conductive polymer composite can be produced by loading an insulating polymer matrix with a sufficient volume of an electrically conductive filler [1], so that interconnectivity of conductive pathways exists throughout the bulk material. As a result, the percolation threshold of the filler in the matrix is exceeded [2,3], and in the case of relatively inexpensive high-structure carbon blacks [4], this can be achieved at a relatively low volume loading. This enhances the processability of the material and ensures the cost of the conductive polymer composite remains appealing.

In addition, these composites can behave as a very non-linear positive temperature coefficient (PTC) resistors [5,6]; a property that has been exploited in a number of smart-material applications including self-regulating heating cables [7] and resettable fuse devices [8,9].

In the case of a resettable fuse, the device is designed to conduct a moderate current in a particular voltage regime, during which it is said to be operating in the 'untripped' or passive state. However, if a fault develops, such as a short-circuit, an abnormally high current would flow. This results in excessive energy dissipation due to internal resistive heating, and would rapidly warm the polymer matrix above its melting temperature, forcing a marked expansion of the polymer and the breaking apart of the conductive network [10]. This effectively prevents the high electric current from flowing by presenting a high resistance. The device is then said to be in a 'tripped' or active state. However, when the fault passes, the polymer matrix cools, and the electrical conductive pathways are re-established. The stability of this property can be enhanced by chemical or radiation cross-linking of the polymer composite [11,12].

In reality the process described above is more complex, because any breakage of a conductive pathway in the composite instantly reduces the local current, and causes the matrix to cool and contract. However, as soon as two neighbouring carbon black particles re-establish contact, the surge in electrical current and the consequential re-heating of the material would cause localized expansion and re-breaking of the circuit. This dynamic equilibrium would occur throughout the region of the material where the rate of heat loss is the lowest, and this region is termed the 'hot-plane'. Consequently, the device remains in the 'tripped' state until the fault passes.

However, despite this broad understanding of conductive polymer composite resettable fuse devices, it is still difficult to quantify their inherent stability over many such 'trip-cycles'. In particular, it has not been clear if morphological changes occur during the life of a device and if the active hot-plane migrates with time. It would also be interesting to be able to detect the position of the hot-plane and determine if it remains consistent throughout a batch of similar devices.

In this paper, a technique is exploited that enables the position of the hot-plane to be determined and investigated. It stems from the fact that across the hot-plane of a tripped device, the potential will drop from the applied voltage to very close to zero. This is due to the high electrical resistance of the broken network. Where the hot-plane impinges on to a surface, there is a 'hot-line' across which the electrical field changes. Hence, it is possible to detect this by using voltage contrast scanning electron microscopy (VC-SEM) [13].

In the past, this technique has been applied to understanding the operation and quality control aspects of integrated circuits [13]. When a region has a positive voltage bias relative to a neighbouring region at ground, the positive region appears darker because it reduces the electric field

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* To whom correspondence should be addressed. Present address: School of Electronic and Electrical Engineering, Information Technology and Mathematics, University of Surrey, Guildford, Surrey, GU2 5XH, U.K. Te: +44 (0)1483 300800 x2289, Fax: +44 (0)1483 534139, E-mail: a.burden@ee.surrey.ac.uk

created by the biased secondary electron detector. Hence, secondary electrons from these regions are collected less efficiently. This leads to contrast at the hot-plane of a tripped conductive polymer composite, and is illustrated schematically in *Figure 1*. It is exaggerated by utilizing low voltage SEM which increases the yield of secondary electrons and reduces specimen charging [14]. Increasing the voltage bias of the collector and tripping the device with a modest voltage can also lead to improvements. However, the effects on the microscopy do need to be appreciated. For example, highly biased or charged samples and biased detectors will distort the image created by a low-voltage SEM, and reduce the apparent spatial resolution of the instrument [14].

EXPERIMENTAL

Investigation of devices

PolySwitch® resettable fuses (type RXE050, illustrated in *Figure 2* and obtained prior to epoxy-encapsulation from Raychem Ltd.) were prepared for examination by slicing away sections of the devices with a sharp razor blade to leave a flat surface. The angle of a slice was set to be parallel to the secondary electron detector in the SEM. This optimized the collection of the electrons used to create the image, reducing image skewing and loss of intensity. The ability of a device to continue to operate after removing a portion of it reflected the intrinsically smart nature of the material.

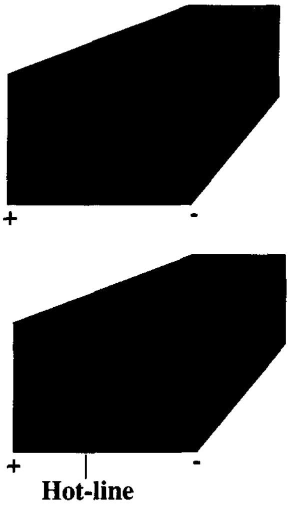

Figure 1 A schematic of an un-tripped and tripped device, with the carbon black aggregates greatly exaggerated. In the latter case, voltage contrast is seen in the SEM

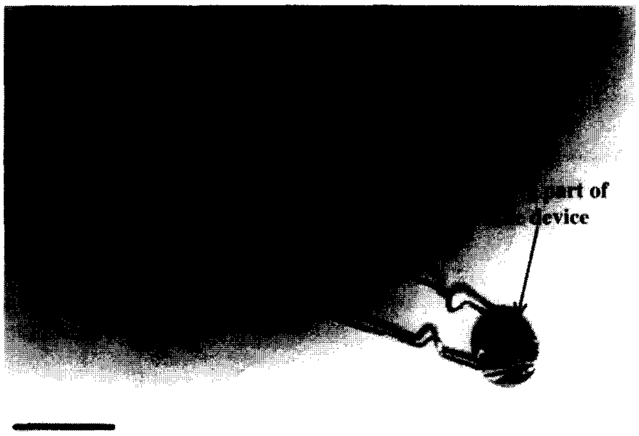

Figure 2 The RXE050 PolySwitch® device prior to epoxy-encapsulation, showing the electrodes that sandwich the conductive polymer composite in the active part of the device. Scale bar = 1 cm

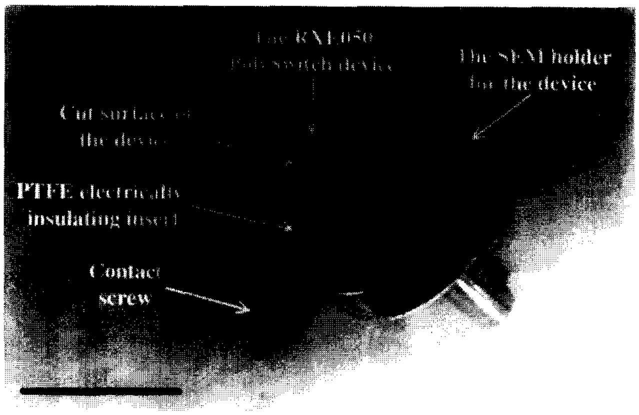

Figure 3 The SEM holder designed for electrically operating the PolySwitch® device *in situ*. Scale bar = 1 cm

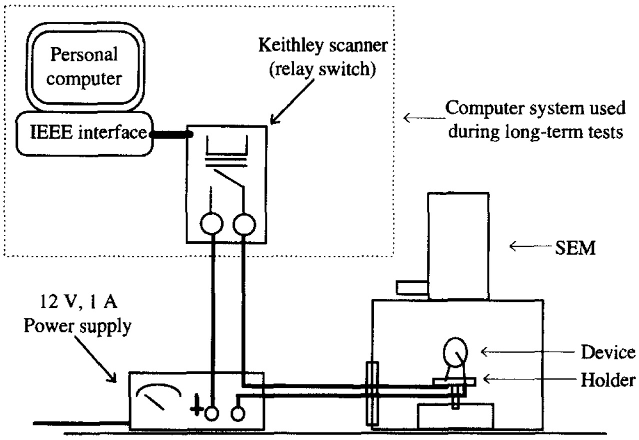

Figure 4 A schematic of the circuit used to power the device during *in situ* SEM experiments. The computer system enclosed in the dotted lines was used for the automated long-term tests

A sample holder was designed to allow the *in situ* operation of a resettable fuse device while being investigated with the SEM. This is illustrated, with a prepared device in place, in *Figure 3*. The holder was connected to an external power supply via an electrical port on the microscope specimen chamber. A schematic of the circuit is shown in *Figure 4*.

The microscope used was a Cambridge Instrument Stereoscan 250 Mk3 SEM. It was usually operated at 5 kV, using a tungsten filament. The secondary-electron detector was used with a positive bias of ~50–200 V applied. Images were digitally recorded using a 'frame-store' card on a personal computer. In order to trip the device, 12 V and 1 A was applied by closing the power supply switch in the circuit. Several experiments were then performed on different devices, aimed at exploiting the imaging technique and the SEM in general.

Investigation of conductive polymer composite material

The PolySwitch® device described above has been through many processing steps to give a reliable and complete component, including thermal processes that

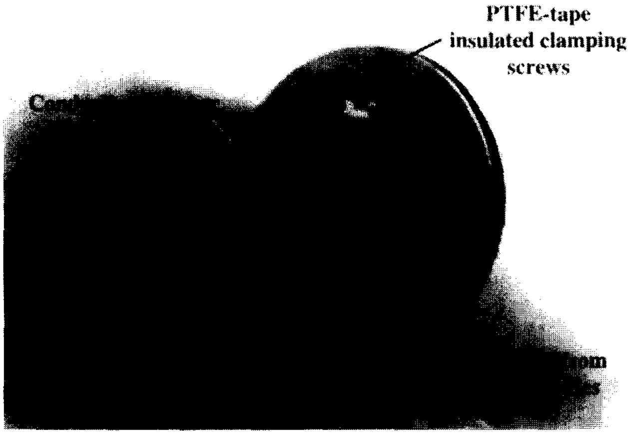

Figure 5 The 'flower-press' SEM holder designed to clamp a 1 cm^2 plaque of conductive polymer composite material between electrodes for operation *in situ*. Scale bar = 1 cm

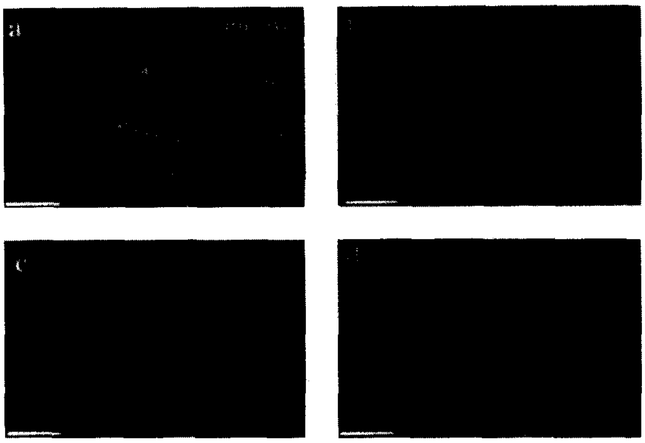

Figure 6 The top surface of a prepared PolySwitch® device, showing the asymmetric layout of the electrode legs and the voltage contrast of two subsequent trip cycles. The device was untripped in (*a*), tripped in (*b*), untripped in (*c*) and tripped again in (*d*). Scale bars = 1 mm

greatly modify the microstructure of the material and affect its electrical properties.

Hence, an investigation was performed on some conductive polymer composite material which had been pressed into thin plaques, without any subsequent processing steps. Because this material functioned as a PTC resistor [15], it was hoped that a hot-line investigation could be achieved without the added complications of other processing steps [16] and any attached electrodes.

A sample holder was designed to allow *in situ* operation of the conductive polymer composite while being investigated with the SEM. It has been dubbed the 'flower-press', and was designed to squeeze lightly a 1 cm^2 plaque of material and provide electrical contact to its surfaces, as illustrated in *Figure 5*.

In order to make good electrical contact with both faces of the thin plaque, several techniques were attempted. Lamination of the plaques was avoided because of the extra processing step that it would introduce, complicating the material's thermal history, and making surface preparation more difficult (as discussed later). Silver paint or electrodag was also foubd unsuitable as a surface conducting coating, because it was unable to expand sufficiently with the polymer during cycling. This resulted in the dramatic loss of adhesion of the layer, and buckling and cracking at the electrode/composite interface. The solution adopted was to sputter-coat a thin layer of gold on to each surface. This process was thought not to have raised the temperature of the material very significantly.

The surface of the sample was then prepared by either cutting with a sharp razor blade, or by using a glass knife cryo-microtome, which gave much smoother surfaces and was suited to preparation of the conductive polymer composite with the gold-sputtered electrodes. It had not been possible to microtome the PolySwitch® devices because of the attached thick metal electrodes.

The conductive polymer composite was then introduced into the SEM and operated as described earlier. In order to trip the composite material, 12 V and 1 A were applied by closing the switch in the circuit. Several experiments were then performed on different samples.

RESULTS AND DISCUSSION

Single-trip images of devices

The first device was imaged while no current was flowing, as shown in *Figure 6a*. Then it was tripped by applying 1 A and 12 V. The resulting voltage contrast on the device was then observed and recorded, as shown in *Figure 6b*, before the current was turned off, allowing the device to become untripped. This is shown in *Figure 6c*, before a second trip was performed and imaged (*Figure 6d*).

It is not possible to claim these were the first and second trips of the device, because even a 'new' device may have been tested during production. However, the images in *Figure 6* show that a tripped device investigated *in situ* would give rise to the expected voltage contrast, interpretable as the hot-plane intersecting the surface as a hot-line.

It also showed that the hot-line was not necessarily straight and central. This is believed to be due to the heat-sink effect of the attached electrodes modifying heat flow from the bulk. In particular, the asymmetric position of the soldered legs and their subsequent fixing in the SEM holder would have removed heat from the device non-uniformly across its cross section. Heat was withdrawn more efficiently from the regions nearest the leg, which had the effect of pushing the hot-line on that cross section further away from it. Any off-centring of the overall hot-plane in the material would, therefore, have been due to heat being removed from the device more efficiently from one electrode than the other. This was probably due to better thermal contact with the SEM holder through the electrical connections, rather than any variation in the electrode with the polymer. It also illustrated the short-term stability of the device, as in the subsequent trip, the hot-line was seen in the same location.

Figure 7 is a montage of different devices showing the voltage contrast when the devices were tripped with 12 V, 1 A. In each case, the electrode legs are seen to modify the position and shape of the hot-line in a similar way. Note that the angle of the prepared surface with respect to the bulk varies with each device, and so the thermal effects will also be changed. In no case is the hot-line straight or centrally located. *Figure 7e* also clearly shows voltage contrast on the unprepared edge of the device (visible to some extent in parts *a*, *b* and *c*).

Reversed-polarity trips of devices

The resettable fuse device is capable of working regardless of the direction of the applied current. Hence, a fuse tripped by a reversed-polarity voltage should give a hot-plane in the same location as the original trip, but with a negative voltage contrast. This was confirmed to be the case, although not illustrated in this paper, and means that the technique for locating and investigating the position and stability of the hot-line is reliable and independent of the polarity of the applied voltage.

Multiple-trip images of devices

Because the SEM builds up an image by simultaneously rastering over the specimen and the monitor, it was possible to slow down the scan speed and trip the device several times during a single image frame.

Figure 8 shows the voltage contrast on part of a device when tripped for the duration of the image scan. This is the same approach as used in *Figures 6 and 7*. However, *Figure 8b* illustrates the effect of tripping and untripping the device during a single scan and shows several important contrast features.

Firstly, the hot-line remained stable during each trip cycle as, when tripped, the voltage contrast occurred where it would be expected through comparison with *Figure 8a*. This would be expected from the short-term stability seen earlier, although in this case, the stability is seen over at least four cycles.

The narrow region of intermediate contrast that separated the untripped and tripped states was when the device was 'powered-but-untripped'. This was due to a minimal and gradual voltage drop across the device which was somewhere between 0 and 12 V. The finite time for the device to trip can thus be deduced from the scan-speed of the SEM. Sometimes the width of this contrast feature narrowed with successive trips, which implied the device was tripping faster. This was because the device was already warm from the previous trip, and so took less time to respond to the next. The switching time was reduced and the reset time extended because of the poor thermal conductivity of the vacuum in the SEM. Hence, heat transfer was primarily by conduction through the electrodes rather than by convection with the surrounding environment.

In *Figure 8*, the SEM image was acquired over a period of 66 s. Hence, from measurement of the second 'tripping' band, the device took ~1.4 s to trip in this environment. This demonstrates that the quantitative information that can be gained from this technique should be useful in assessing the relative trip speeds of devices. Although the vacuum environment is not thermally equivalent to atmospheric service environments, it could provide a uniform set of conditions with which to bench-mark a series of device configurations and investigate their untripped through tripping to tripped behaviour.

Multiple-trip long-term stability tests of devices

A software program was designed to operate the trip-switch automatically via an IOTech IEEE488 hardware control card installed in a personal computer, and an attached Keithley 705 Scanner. It was designed so that it was possible to use the cycling routine with the image acquisition software simultaneously. The set-up is as illustrated in *Figure 4*, but now including the system enclosed by the dotted lines.

This enabled the device to be tripped automatically thousands of times in rapid succession (approximately 10 s on, 10 s off), while it remained in the SEM. During the extended cycling, electron-beam damage was minimized by turning off the SEM electron-beam. The vacuum was, however, maintained. The advantage of keeping the device

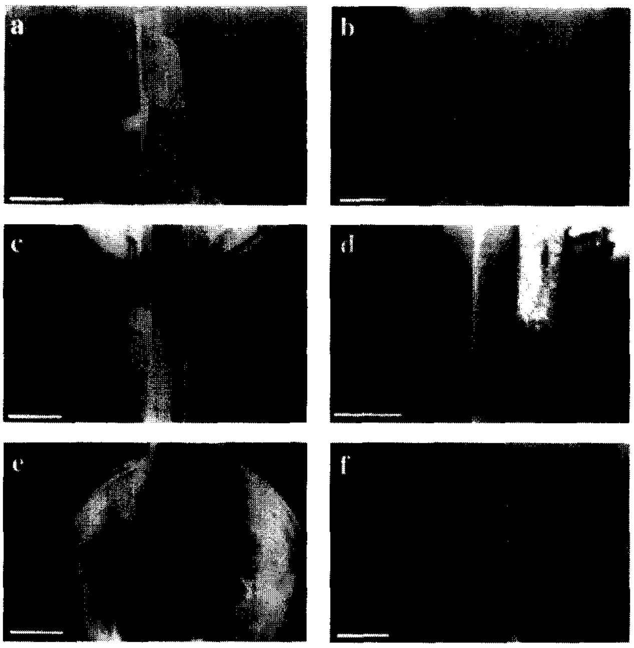

Figure 7 A selection of devices exhibiting voltage contrast when tripped with 12 V, 1 A. In each case the surface was prepared with a sharp razor blade, and the SEM was operated at 5 kV (except *c* which was 2.5 kV). Scale bars = 1 mm

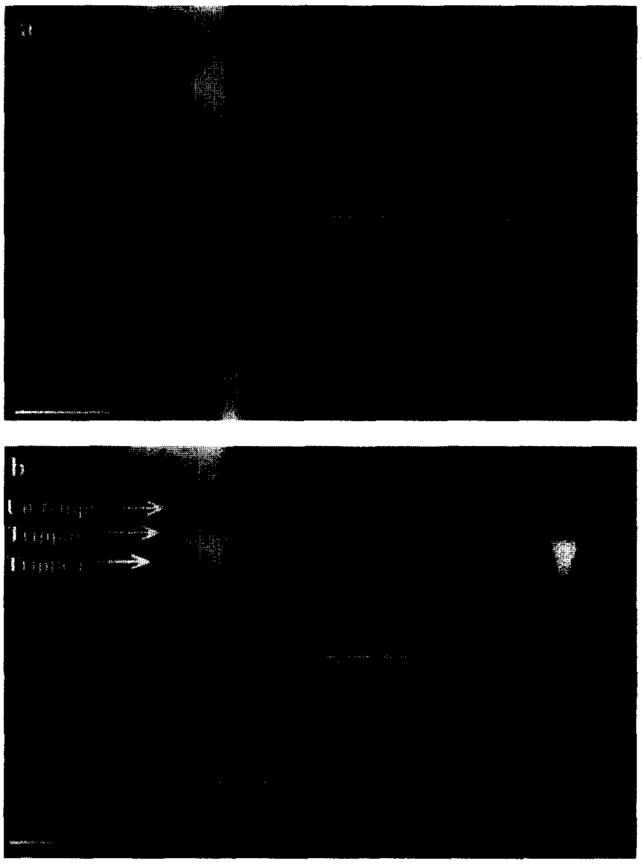

Figure 8 The image showing voltage contrast on a tripped device (*a*) is obtained with an SEM by building up the image with a slow scan over the specimen. This can be exploited (*b*) so that untripped, tripping, and tripped states are recorded in series on the same image. This provides information on the stability of the hot-line and the switching times between untripped and tripped states. Scale bars = 400 μm

in the SEM was that each image after many trips would be at the same angle and position as the previous image. This meant direct comparisons could be made as no topographical contrast variation could occur. However, the disadvantage was that it tied-up a SEM for long periods of time (over 2 weeks for the long-term test described here).

Figure 9 illustrates the voltage contrast seen on a device during the long-term test. In *Figure 9a* and *b* it is seen during its second and third drips, respectively (excluding any performed during manufacture). In *Figure 9c*, it had been left to trip a further 10 times using the software control program, and then it was tripped again to view the voltage contrast of the hot-line. *Figure 9d* was taken after a further 100 trips (+ 1 to view), *Figure 9e* after a further 24 210 trips (+ 1 to view), and part *f* after a further 34 000 trips (+ 1 to view). Note that the latter two entailed a continuous operation of the device for over $5\frac{1}{2}$ days and over $7\frac{1}{2}$ days, respectively.

However, it is immediately apparent that the stability of the hot-line was good over the 58 000-or-more cycles, and that its position and shape did not noticeably change. Although such a result may be expected, because devices of this sort are designed to operate for many thousands of cycles, it is the only known visual evidence to confirm that the inherent reliability of the device is characterized by a stable hot-line during a significant portion of its life.

In/out trial of devices

Also of interest was whether the hot-line could be reviewed when the device had been taken in and out of the SEM and its holder. This was successfully performed on the device used in the previous section; the result being important if very long-term tests are performed and the SEM cannot be out of general use for so long. For example, a device could be tripped continually for many months and then re-analysed to see if any hot-line drift had occurred. Because of the time scale of this kind of test, it has not been included in this study.

However, during this investigation, the current of an operating tripped device was seen to fall while the SEM was pumping down in preparation for a review of the hot-line. For example, one device was operating at 12 V, and drawing ~90 mA in the room environment. However, as pumping commenced, it was seen to fall to ~65 mA as the turbomolecular pump achieved base column pressure. This can be explained by the thermal effects of the environment. As the vacuum improved, so the loss of heat from the device to the surroundings by convection was reduced, and the device became warmer and more resistive. This shows the importance of the heat-loss mechanisms for defining the characteristics of the device, and the fact that a device could behave differently in the vacuum environment of the SEM.

Demonstration of voltage contrast on conductive polymer composite material

Voltage contrast was achieved on samples of conductive polymer composite, and two examples are illustrated in *Figure 10*. One was prepared with a razor-blade (*a*) and the other with the microtome (*b*). The latter did give the better surface finish, reducing the topographical contrast of the SEM image and thus enhancing the voltage contrast. The figures also indicate the various parts of the holder when seen *in situ*.

The hot-line was seen to run parallel to the edge of the device, and showed no curves or deviations that were attributed to the electrode legs in the case of the

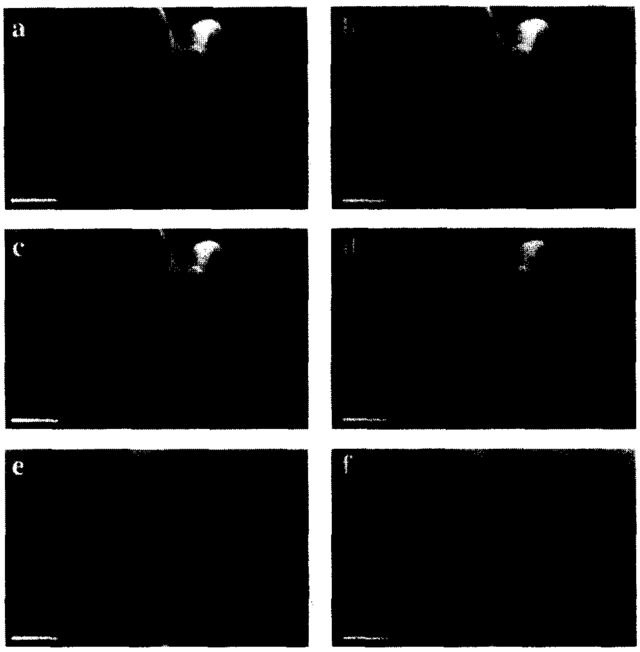

Figure 9 A long-term test of a PolySwitch® device confirms the stability of the hot-line. The device is pictured in a tripped state after approximately (*a*) 1, (*b*) 2, (*c*) 10, (*d*) 110, (*e*) 24100 and (*f*) 58 100 trip cycles. Scale bars = 1 mm

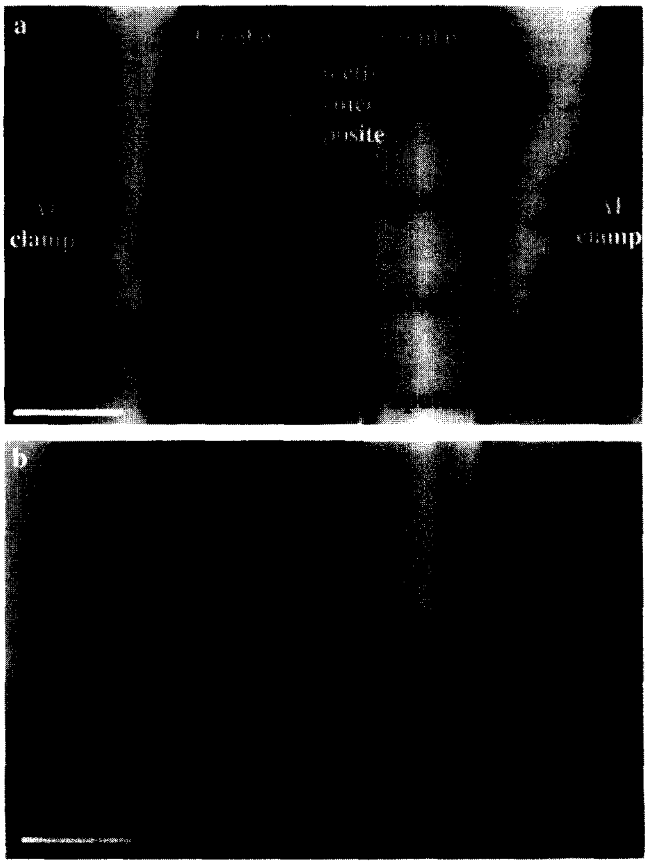

Figure 10 Two examples of the hot-line on samples of conductive polymer composite, when mounted in the 'flower-press'. Nickel metal tabs were used to improve the electrical connection between the copper plates of the holder and the gold surface of the material. This was seen when tripped with 12 V, 1 A in the SEM. Scale bars = 1 mm

PolySwitch® device. This was in good agreement with discussions held earlier. Also, the position of the hot-line was not necessarily central, because of different thermal contact with the holder on one side of the material from the other. In fact, it was sometimes quite difficult to trip the conductive polymer composite because, if the 'flower-press' was squeezed too tightly, it was too effective at removing the heat from the device or it would not allow the material to expand sufficiently to produce the increase in resistance. Conversely, when the grip was poor, the electrical contact was erratic and sparks destroyed the gold layer on the surface. Therefore, the material was somewhat subjectively mounted in the holder.

However, because this was previously untested material, it was now possible to know the number of cycles the material had been through. In the cases in *Figure 10*, these were seen after the second trip, as the first was conducted before the SEM was evacuated to ensure there was adequate electrical contact.

Capabilities for morphological studies

The main purpose of performing the tests on the conductive polymer composite was to demonstrate techniques that could be used to learn more about the morphology of the composite and, in particular, any differences between the active region of the device and elsewhere.

Figure 11 shows the best resolution achievable with this SEM while the device was operating. The voltage contrast is not seen, because at higher magnification, topographical contrast becomes more significant. However, this was in the vicinity of the hot-line seen in *Figure 10a*. The features are interpretable as carbon black aggregates, being approximately 500 nm in size. However, it is clear that very little useful morphological information was forthcoming.

Another approach would be to record the position of the hot-line from the voltage contrast and then transfer the sample to a microscope of improved performance for the morphology study.

In the example reproted here, the material was also prepared for a morphological investigation of the carbon black. In this case, the surface of interest was etched using a solution partly containing concentrated sulphuric acid[17]. This selectively removed a thin layer of polymer from the surface, leaving the carbon black aggregates in place. This could not be performed on the PolySwitch® devices

Figure 11 A higher magnification image of the area of the hot-line of an operating device. The features can be interpreted as the carbon black aggregates in the polymer matrix, but the detail of the morphology is not great. Scale bar = 4 μm

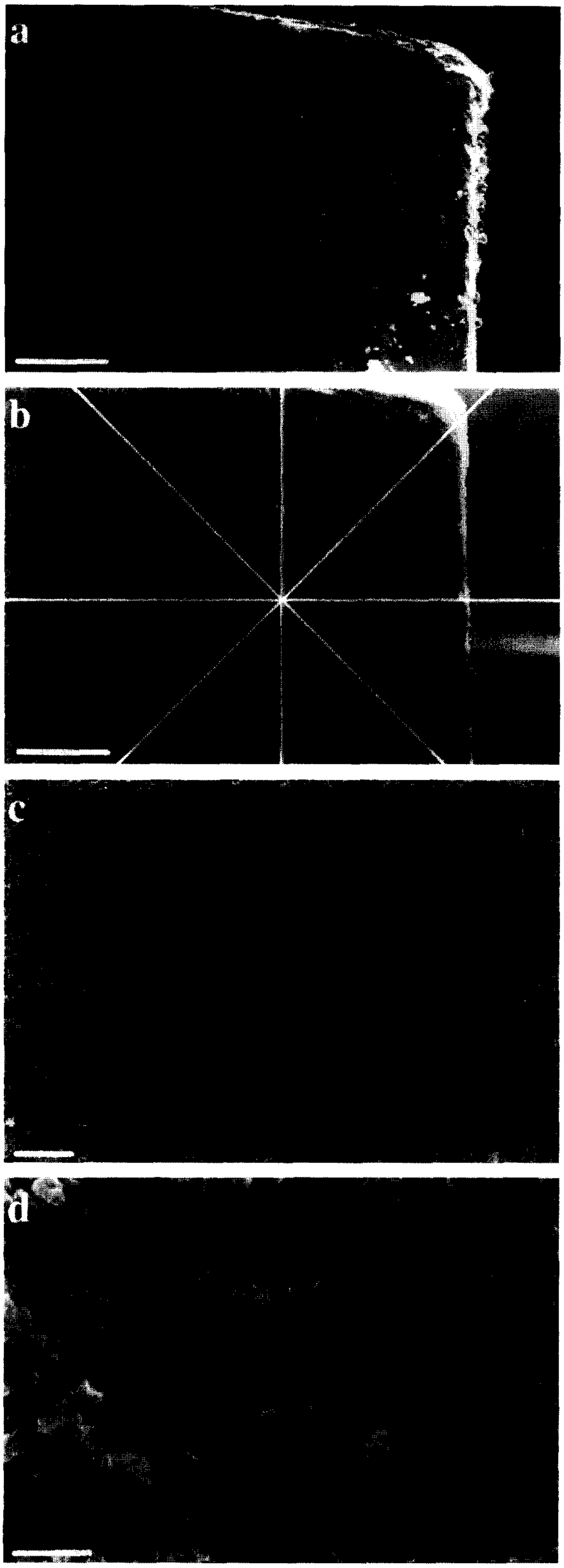

Figure 12 The region near the identified hot-line (*a*) is marked by cross-hairs in another SEM after chemically etching the surface (*b*). Scale bars = 100 μm. Further detail of the hot-line region is shown in (*c*). Scale bar = 10 μm. The carbon black aggregates are also clearly seen (*d*) because the surface polymer has been etched away. Scale bar = 1 μm

investigated previously, because the metal electrodes poisoned the etch-solution. The surface was then lightly coated in carbon for viewing by conventional SEM. The SEM used was a Cambridge Stereoscan 440 instrument fitted with a LaB_6 filament and oeprated at 20 kV.

Figure 12b shows that the earlier area (*a*) was relocated, and the cross-hairs mark the position where the active region was previously identified by the hot-line. This etched region is seen in greater detail (*c*), and by way of illustration, the carbon black primary particles are imaged in (*d*).

By identifying the hot-line it was possible to probe the region in more detail, and study its morphology. In this case, comparison with other areas did not lead to any significant differences being identified. It was suspected that the polymer, rather than the carbon black distribution or morphology, would have become modified at the active region. Hence, a future study would need to be performed on unetched but possibly stained material.

CONCLUSION

Voltage contrast SEM has been exploited to investigate the position of the hot-plane in a number of powered resettable fuse devices. Various experiments have been employed to show that the position of the hot-plane on the surface of the composite is stable with successive trip-cycles. It has also shown that this position is consistent with operation in reverse-polarity and that irregularities in the shape of the hot-plane can be explained by surface heat-sink effects and the position of electrodes.

Conductive polymer composite material has also been investigated, and the ability to investigate the hot-line demonstrated. In this case, a substantial amount of developmental work has shown that sputtered gold layers form the best electrodes if the thermal and mechanical process of attaching more permanent electrodes is to be avoided.

The ability to identify the active region should enable more to be learnt about the morphology of the material. It was found that the carbon black distribution was not significantly altered near the hot-line, but it is suspected that the polymer would show microstructural differences. Further development of this technique should provide a means of investigating this aspect of conductive polymer composite devices in more detail.

ACKNOWLEDGEMENTS

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PolySwitch® is a trademark of Raychem Corporation.

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