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(54) Title: ELECTRIC-FIELD ENHANCED PERFORMANCE IN CATALYSIS AND SOLID-STATE DEVICES INVOLVING
GASES

(57) **Abrégé/Abstract:**

Electrode configurations for electric-field enhanced performance in catalysis and solid-state devices involving gases are provided. According to an embodiment, electric- field electrodes can be incorporated in devices such as gas sensors and fuel cells to shape an electric field provided with respect to sensing electrodes for the gas sensors and surfaces of the fuel cells. The shaped electric fields can alter surface dynamics, system thermodynamics, reaction kinetics, and adsorption/desorption processes. In one embodiment, ring-shaped electric- field electrodes can be provided around sensing electrodes of a planar gas sensor.



Abstract

Electrode configurations for electric-field enhanced performance in catalysis and solid-state devices involving gases are provided. According to an embodiment, electric-field electrodes can be incorporated in devices such as gas sensors and fuel cells to shape an electric field provided with respect to sensing electrodes for the gas sensors and surfaces of the fuel cells. The shaped electric fields can alter surface dynamics, system thermodynamics, reaction kinetics, and adsorption/desorption processes. In one embodiment, ring-shaped electric-field electrodes can be provided around sensing electrodes of a planar gas sensor.

DESCRIPTION

ELECTRIC-FIELD ENHANCED PERFORMANCE IN CATALYSIS
AND SOLID-STATE DEVICES INVOLVING GASES

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BACKGROUND OF INVENTION

An electrochemical cell is the coupling of two electrode materials between an ionic conductor, whereby electrochemical reactions occur at the interface between the ionic conductor, an electrode, and gas. The electrode materials are typically metal or semiconductor and the ionic conductor is typically an electrolyte. Electrodes may also include mixed electronic/ionic materials. Currently, yttria stabilized zirconia (YSZ) is being used as the electrolyte material for certain gas sensors and fuel cells.

Electrochemical cells may operate in open-circuit mode or may be used to drive reactions with the application of current or voltage to the cell. Electrochemical cells are used in many devices, such as gas sensors and fuel cells, and applications, such as electroplating. Electrochemical cells are also used in catalysis for the conversion of reactants into useful byproducts.

A gas sensor is a device that detects the concentration or presence of a single or multiple gas species. A gas sensor may, but need not, include an electrochemical cell. A gas sensor without an electrochemical cell can be considered a non-electrochemical device. A gas sensor may have different transduction mechanisms for detecting gas and may be multifunctional by detecting multiple gas species. For example, potentiometric, amperometric, or impedancemetric transduction mechanisms may be used. One issue with most gas sensors is cross-interference from other species, or poor selectivity.

A fuel cell is a device that directly converts chemical energy into electrical energy for power consumption in applications such as for automobiles and homes. A solid oxide fuel cell (SOFC) is one type of fuel cell that incorporates a solid electrolyte sandwiched between at least two electrodes, one electrode functioning as a cathode and the other electrode

functioning as an anode. Fuel cells may also be incorporated into stacks in order to increase power output. In the case where the electrolyte is an oxygen ion conductor, oxygen reacts at the cathode and is transported to the anode through the electrolyte as an ion where the oxygen electrochemically reacts with fuel, such as, for example, H_2 or CO , to produce electricity.

5 In certain devices using electrochemical cells, Non-Faradaic Electrochemical Modification of Catalytic Activity (NEMCA) is incorporated for the enhancement of catalytic reactions through the direct application of voltage or current to the electrodes in an electrochemical cell.

10 In catalysis, the kinetics of a reaction involves the process of changing rates of intermediate steps and other processes during a reaction. These changes affect the overall reaction rate.

15 The energetics of a reaction refers to the many different energy barriers to activating the steps of a reaction. As an example, a diffusion barrier is one type of energy barrier. These barriers can be overcome by adding energy to the system. Often thermal energy is used to overcome the barriers.

20 A reaction pathway is the steps that a reaction follows as it proceeds from starting reactants to final products. The pathway that a reaction follows has to do, in part, with the kinetics and energetics of the system. Adsorption and desorption are processes where gas molecules from the gas phase are trapped (physisorption) or bonded to the surface (chemisorption). These processes often also affect the kinetics and energetics of a reaction.

25 Surface relaxation involves the motion of entire adlayer(s), while surface reconstruction involves changes in the surface periodicity. Both processes can change the way a reaction proceeds. Surface dynamics may refer to the processes that involve dynamic motion on a surface, such as gas (phase) molecules colliding with a surface or diffusion of a species on a surface.

 A catalyst may exist as part of an electrochemical device or atop a “catalyst support” which acts to either provide a certain structure for the catalysts or to disperse the catalyst among different reaction sites.

30 One major problem in catalysis is diminished conversion due to the presence of “poisons.” The presence of “poisons” can also have negative impacts in gas sensors, fuel cells, and other related devices. Poisons may block adsorption sites or cause phase reconstruction; the latter case may be caused by poisons forming complexes with, for instance, oxygen species from an electrolyte, and possibly followed by desorption of the

complex. This may prevent certain mechanisms from occurring that rely on the presence of that oxygen, thereby inhibiting the device or catalyst from performing properly.

BRIEF SUMMARY

5 Embodiments of the present invention relate to electric field enhancement of chemical and/or electrochemical reactions. An electric field can be produced and shaped to alter gas adsorption and other chemical reactions for various applications. The generated electric field can be provided using electric-field electrodes, which are conductive surfaces purposefully biased so as to generate an electric field. Certain embodiments of the present invention can
10 be applied to gas sensors, fuel cells, and other electrochemical devices. In addition, certain embodiments can be used to improve the performance of electrochemically promoted reactions (NEMCA) and any other general catalysis reaction involving at least one gaseous species, such as, for example, ethylene oxidation. Electric-field electrodes arranged according to an embodiment of the present invention can also be applied to non-
15 electrochemical devices such as gas sensors that do not utilize an electrolyte.

 In an embodiment, electric-field electrodes can be applied to a gas sensor. The electric-field electrodes can be arranged to improve sensitivity, selectivity, and response time in the gas sensor.

 In one embodiment, the electric-field electrodes can be positioned to apply an electric
20 field parallel to a sensing electrode of the gas sensor.

 In another embodiment, electric-field electrodes can be applied to a gas sensor for shaping the electric field profile. In such an embodiment, electric-field electrodes can be positioned with respect to the sensing electrodes of the gas sensor to apply a desired electric field profile with respect to specific locations on a device or catalyst support. The electric
25 fields can be shaped to be perpendicular, parallel, or any angle in between with respect to a particular local reaction zone or entire device. In addition, the relative strengths of the electric fields at different regions of the device can be different. In a further embodiment, the electric-field electrodes can be applied to a gas sensor incorporating an air-reference electrode.

30 In an embodiment, electric-field electrodes can be applied to a fuel cell. The electric-field electrodes can be used to stabilize/destabilize adsorbate complexes on a surface and remove or inhibit buildup of poisons from a fuel cell surface.

Electric-field electrodes arranged according to an embodiment of the present invention can be applied for altering the localized fields that exist around a dipole layer region in an electrochemical system using the externally generated electric fields.

“Electric-field electrodes” may be used to enhance chemical/electrochemical reactions and performance in various devices and applications. Such “Electric-field electrodes” may be effectively and actively shaped to achieve enhanced performance. In embodiments for electrochemical devices, little or no (ionic or electronic) current or charge is introduced to the metal/electrolyte or semiconductor/electrolyte interface. Furthermore, the such “Electric-field electrodes” may incorporate any other structure or component of the device that has at least one additional purpose other than to contribute to the shape of the electric field.

Voltage may be applied with a battery or other voltage source where more than one voltage source may be used if desired. One or more voltage signals may be distributed with a microcontroller, multiplexer, (resistive) voltage divider, and/or other means of applying different voltage magnitudes or bias schemes to various “electric-field electrodes”.

There are numerous techniques that can be employed in the manufacture of these devices. Multiple devices may be made simultaneously and separated by various means after manufacture. Furthermore, these and other techniques may be used to deposit catalysts on electric-field enhanced catalyst supports. Any combination of the following techniques or other techniques known to those skilled in the art may be used:

20

i) *Multilayer Fabrication*

tape-casting, screen-printing;

ii) *Bottom-Up (additive) Approach*

direct-write methods (e.g., pump- or aerosol-based deposition), dip coating, spin coating, laser sintering;

25

iii) *Multi-step (subtractive) Approach*

microfabrication using photolithography and other techniques used in the fabrication of microelectronics and microelectro-mechanical systems (MEMS), electron-beam and laser-based subtractive fabrication, laser micromachining;

30

iv) *Wire Attachment Methods And Metallization*

metals used for metallization or wire attachment are preferably able to withstand harsh environments, wire bonding (e.g., Au or Pt wire), brazing, and/or any other method of

wire attachment. Different metallization may exist in multiple layers and connected to each other by vias that exist in between layers;

5 v) *Device Packaging*

standard or new packaging techniques and designs of high-temperature (or any other) electronics and/or sensors may be used with this device; and

 vi) *Catalyst Deposition*

10 catalyst materials may be deposited onto supports using any method such as spin coating, dip coating, or thermal spraying.

Embodiments of the subject invention can be directed to performance enhanced gas sensors, fuel cells, and other electrochemical or non-electrochemical devices, enhanced catalytic reactions in chemical processing and improved catalytic converters. Embodiments can achieve lower costs, increased productivity, efficiency and/or accuracy depending on the application, including automobile manufacturers, sensor companies, electric utility companies, and/or chemical manufacturing companies.

BRIEF DESCRIPTION OF DRAWINGS

20 **Figures 1A-1C** show a planar gas sensor according to an embodiment of the present invention. Figure 1A shows a cross-sectional view of the planar gas sensor with electric field applied parallel to the sensing electrodes according to an embodiment of the present invention, Figure 1B shows a top view of the planar gas sensor of Figure 1A, and Figure 1C shows a bottom view of the planar gas sensor of Figure 1A.

25 **Figures 2A-2C** show a planar gas sensor according to an embodiment of the present invention. Figure 2A shows a cross-sectional view of the planar gas sensor with electric-field electrodes for actively shaping the electric field according to an embodiment of the present invention, Figure 2B shows a top view of the planar gas sensor of Figure 2A, and Figure 2C shows a bottom view of the planar gas sensor of Figure 2A.

30 **Figures 3A-3B** show plots comparing changes in NO and NO₂ sensitivity with and without the use of the electric-field electrodes (bias scheme 1, Table 2) for a variety of ambient temperatures.

Figures 3C-3D show the results of NO and NO₂ sensitivity for biasing scheme 1 (Table 2) with negative (-) field bias at 500C applied to the embodiment shown in Figures 2A-2C.

Figure 3E shows the sensor response to NO and NO₂ at 500C for biasing scheme 2 (Table 2) applied to the embodiment shown in Figures 2A-2C.

Figure 3F shows NO₂ results for biasing scheme 3 (Table 2) applied to the embodiment shown in Figures 2A-2C, where only the conduction layers 11 and 19 on the La₂CuO₄ side of the device are charged; the other conduction layers are left uncharged.

Figure 3G shows NO results for biasing scheme 3 (Table 2) applied to the embodiment shown in Figures 2A-2C, where only the conduction layers 11 and 19 on the La₂CuO₄ side of the device are charged; the other conduction layers are left uncharged.

Figure 3H shows the results for biasing scheme 4 (Table 2) applied to the embodiment shown in Figures 2A-2C.

Figures 4A-4D show electric field plots of three different actively-shaped electric fields using the planar sensor according to the embodiment shown in Figures 2A-2C.

Figures 5A-5C show a planar gas sensor according to an embodiment of the present invention. Figure 5A shows a cross-sectional view of the planar gas sensor with air-reference electrode according to an embodiment of the present invention, Figure 5B shows a top view of the planar gas sensor of Figure 5A, and Figure 5C shows a bottom view of the planar gas sensor of Figure 5A.

Figures 6A-6B show mass spectrometry comparisons of the changes in NO_x concentrations coming off the semiconducting material for various applied field voltages during exposure to gas feed compositions of 650 ppm NO or NO₂ at various temperatures, according to the embodiment shown in Figures 5A-5C.

Figures 6C-6D show sensitivity plots of the planar gas sensor according to the embodiment in Figures 5A-5C to NO and NO₂ and the corresponding changes in NO_x concentrations during the 650 ppm feed composition, all at 450C. Figure 6C shows a sensitivity plot and NO_x levels for a sensor exposed to NO, and Figure 6D shows a sensitivity plot and NO_x levels for a sensor exposed to NO₂.

Figures 7A shows schematic of a sample used for temperature programmed desorption (TPD) tests.

Figures 7B-7E show plots of desorption profiles. Figures 7B and 7C show desorption profiles for measured NO and NO₂, respectively, with initial adsorption of NO at 300 °C

according to an embodiment of the present invention, and Figures 7D and 7E show desorption profiles for measured NO and NO₂, respectively, with initial adsorption of NO₂ at 300 °C according to an embodiment of the present invention.

Figures 8A-8F show various other possible configurations for devices (including gas sensors) utilizing the electric-field enhancements. Figure 8A shows a top view of a substrate (electrolyte or other material), with each sensing electrode surrounded with a number of “electric-field electrodes” forming a dashed ring shape around the sensing electrodes. Figure 8B shows the cross-section of 8A, with the sensing electrodes and “electric-field electrodes” displayed on one surface and heater structures (serpentine or other pattern) on a second surface. Figure 8C shows the cross-section of 8A, but now with the “electric field electrodes” and heater structures embedded within the substrate, and a new layer (electrolyte or other material) between the substrate and sensing electrodes.

Figures 8D and 8E show cross-sections of 8A, with heater structures embedded in the substrate and second layer between substrate and sensing electrodes; the electric-field electrodes now form plate-like shapes rather than a dashed arrangement. Furthermore, 8D shows structure that creates a cavity above each sensing electrode; the electric field electrodes are attached to the inner side of this structure. Figure 8E shows a similar cavity-creating structure, but with the electric field electrodes on the top of this structure.

Figures 8F-8H show several additional configurations of devices utilizing the electric-field enhancements. 8F shows the top view of the embodiment with two rectangular layers on top of the substrate containing at least two sensing electrodes each. Several electric field electrodes surround each of these rectangular layers in a dashed arrangement. 8G shows a cross-section of 8F, with rectangular layers and corresponding sensing electrodes and electric-field electrodes. Heating structures are shown on the bottom surface. Figure 8H shows another possible embodiment where one of the rectangular regions with sensing electrodes on top is replaced with a gas sensitive material in contact with the substrate. Electrical contacts are made to this material in two places. The remainder of this embodiment is the same as in 8G.

Figures 9A-9C show an electrochemical device (e.g., a fuel cell) according to an embodiment of the present invention. Figure 9A shows a cross-sectional view of the electrochemical device (e.g., a fuel cell) with electric-field electrodes according to an embodiment of the present invention, Figure 9B shows a top view of the electrochemical

device (e.g., a fuel cell) of Figure 9A, and Figure 9C shows a bottom view of the electrochemical device (e.g., a fuel cell) of Figure 9A.

5 **Figures 10A-10C** show an electrochemical device (e.g., a fuel cell) according to an embodiment of the present invention. Figure 10A shows a cross-sectional view of the electrochemical device (e.g., a fuel cell) with electric-field electrodes in a planar configuration according to an embodiment of the present invention, Figure 10B shows a top view of the electrochemical device (e.g., a fuel cell) of Figure 10A, and Figure 10C shows a bottom view of the electrochemical device (e.g., a fuel cell) of Figure 10A.

10 **Figures 11A-11C** show a catalyst bed according to an embodiment of the present invention. Figure 11A shows a cross-sectional view of the catalyst bed used for catalysis processes according to an embodiment of the present invention, Figure 10B shows a top view of the polygonal-cylinder shape of the catalyst bed of Figure 11A, and Figure 11C shows a representation of catalyst particles.

15

DETAILED DISCLOSURE

Embodiments of the present invention pertain to enhancement of chemical reactions and associated processes through the use of specifically created (or “shaped”) electric fields around the device or location of the reaction or process. The shaped electric fields can be used to improve performance in several applications, including the use in gas sensors, fuel
20 cells, and other electrochemical devices, such as, for example, hydrogen separation membranes. The shaped electric fields can also be used to improve the performance of electrochemically “promoted” reactions such as non-faradaic electrochemical modification of catalytic activity (NEMCA), which are known to enhance catalytic rates through the direct bias of an electrochemical cell. In addition, the “shaped” electric field can be used to
25 enhance any general catalysis reaction involving gaseous species. For example, gas reforming and general catalytic conversion can be enhanced. This includes enhanced performance in other non-electrochemical devices, such as resistive-type gas sensors, or applications such as gas separation, that rely on or utilize gas adsorption or catalytic reactions for some purpose.

30

According to embodiments of the present invention, an electric field can be used to alter gas adsorption and chemical reactions for various applications. The electric field may be generated when a voltage is applied between (at least) two surfaces. Also, multiple voltages may be applied. None of these surfaces needs be local to the device. One of the

surfaces may be ground. A conductive element that is purposefully biased with the applied voltage so as to generate an electric field can be called an “electric-field electrode”.

5 An indirectly-generated, external electric field is created in a way which does not result in the passage of current (electronic or ionic) through a device. In the indirectly-generated electric field, current is blocked by an insulator as in the case of a capacitor and by material that does not conduct ions.

10 A directly-generated electric field, however, is created when a metal or semiconductor has a voltage directly applied to it, whereby electrical current flows through the material. This is also the case when an electrochemical cell is directly biased, except that, at the interface between the electrolyte and metal or semiconductor electrode, the current provides electrons for the electrochemical reaction to occur rather than passing through the device.

15 In the case of an electrochemical cell, an indirectly-generated electric field does not result in charge reaching the electrolyte or electrodes making up the cell. However, a directly-generated field provides charge to the interface of the metal or semiconductor and the electrolyte.

20 According to certain embodiments of the present invention, other parts of the device or catalyst support may participate, either directly or indirectly, in the generation of the electric field. An example of direct participation is where voltage or current is directly applied to a cell as in case of NEMCA. An example of indirect participation is where “natural” field exists in the material.

25 Embodiments of the present invention provide active shaping of an electric field. During active shaping, the electric field distribution may be made uniform or non-uniform, and may be effectively and actively “shaped” to any desired (contour) profile with respect to specific locations on the device or catalyst support (e.g., local reaction zones) or to the entire device/support. The electric fields may be perpendicular, parallel, or any angle in between, with respect to the local reaction zones or the entire device/support. The electric fields may also penetrate any point within the device. Furthermore, the field strengths at various points in the device/support may differ.

30 Electric-field electrodes may be placed in any number and/or arrangement around local reaction zones or the entire device/support. Single or multiple “electric-field electrodes” may be used at any given time. Different layer materials may be used for different “electric-field electrodes” for compatibility with surrounding materials. The “electric-field electrodes” may be provided as single or multiple instances of insulation,

conduction, and cap layers. The number of each layer type for a given “electric-field electrode” need not be the same as the number of layers in other “electric-field electrodes”. The “electric field electrodes” may be imbedded in or on the surface of a device. The “electric field electrodes” may exist in specially designed cavities within the device/support
5 and may incorporate gaps between segments.

The insulation layer for an electric-field electrode acts as a barrier to charge (i.e., electronic or ionic) flow through areas of a device, catalyst, or catalyst support (i.e., substrate holding catalyst) where such current is undesired. The layer may, but need not, participate in chemical and/or electrochemical reactions.

10 The conduction layer of an electric-field electrode acts as a pathway for the charge to reach the (blocking) insulation layer from the source of charge (e.g., power supply). The conduction layer may, but need not, participate in chemical and/or electrochemical reactions. The conduction layer may be formed of conducting materials such as gold (Au).

The cap, or cover, layer of an electric-field electrode acts to keep gas from adsorbing
15 on the conduction layer of an electric-field electrode. The cap layer also acts to further (mechanically) secure conduction layer and insulation layer to substrate. The cap layer may, but need not, participate in chemical and/or electrochemical reactions. The cap layer may, but need not, be formed of insulating materials.

An electric-field electrode may take the form of any geometry such as a square or a
20 circle, including variations in thickness and other dimensions. The geometry of the various layers of the electric-field electrode and layer types may, but need not, be different from each other.

The charge applied to any given “electric-field electrode” may be positive or negative. an “electric-field electrode” may alternatively be grounded or left floating. The electric field
25 “direction” may be altered by changing the location of positive or negative charges, or by changing which “electric-field electrodes” are grounded or left floating.

A fixed (DC) voltage of any magnitude or sign may be applied to the “electric-field electrodes”. The fixed voltage at “electric-field electrodes” may differ from or may be the same as all (or some) of the other “electric-field electrodes”. For any given “electric-field
30 electrode” the applied voltage may be switched between “constant” or “pulsed” biasing schemes. For any given “electric-field electrode” the applied voltage may be switched between “constant” (DC voltage) and (AC voltage) biasing schemes.

Pulsed (DC voltage) electric fields may be generated at different points in time with fixed or varying amplitude and period. In this scheme, the electric fields are pulsed by applying and removing the applied (DC) voltage(s) from all or some of the “electric-field electrodes”. The period and/or amplitude of the pulses may, but need not, be the same for the
5 different “electric field electrodes”. For any given “electric-field electrode” the applied voltage may be switched between “pulsed” or “constant” biasing schemes. For any given “electric-field electrode” the applied voltage may be switched between “pulsed” (DC voltage) and (AC voltage) biasing schemes.

In some embodiments, a time-varying (e.g., sinusoidal) voltage may be applied to the
10 “electric-field electrodes”. For any given “electric-field electrode” the applied voltage may be switched between (AC voltage) and (DC voltage) biasing schemes.

Current and voltage of any “electric field electrode” may be measured by various means at any time to ensure that they continue to work during operation of device or catalyst.

By manipulating the electric field using electric-field electrodes according to
15 embodiments of the present invention, certain mechanisms can be taken advantage of for enhanced performance in catalysis and solid state devices involving gases. The electric field enhancement may result in changes to the frequencies of the molecular bending modes of intramolecular adsorbate bonds or surface-adsorbate bonds. These electrostatic mechanisms can result in changes to bond angles and or bond lengths. In addition, polarization and
20 resultant stabilization, alignment, or changes in orientation of the surface atoms or bulk atoms or in adsorbates (which may be polar species) may also occur.

Chemical mechanisms can include modification of orbitals and in the amount of donation/backdonation. There may be changes in the electron density of the surface and/or adsorbate and changes in the Pauli Repulsion, which may affect stability of complex
25 formation (for charged and uncharged species). These chemical mechanisms may change the strength of intramolecular adsorbate bonds or surface-adsorbate bonds.

In some instances the electric field may result in both electrostatic and chemical mechanisms. There may be equal contribution by both mechanisms, or one may be more dominant than the other. In addition, both the electrostatic and chemical mechanisms may
30 also alter lateral interactions between adsorbates in an adlayer.

In other instances the electric-field may cause changes to the Fermi level(s) of the material(s) involved in the device or process, thereby changing the adsorptive and/or catalytic properties of some or all of the materials.

The resulting changes to a system after the electric-field enhancement may cause several different effects. One effect is the altering of reaction pathways. For example, new reaction pathways may become available as a result of the electric-field enhancement. This may allow improvements in catalytic rates, byproduct concentrations, or new byproducts altogether. The kinetics of a reaction may be shifted to open new reaction pathways, or lower (or raise) the required temperature for reactions to occur.

Another effect is the altering of adsorption/desorption or dissociative/recombinative processes. For example, the adsorption of reaction inhibitors (or “poisons”) may be prevented from accumulating or caused to desorb in a desirable way. Reaction promoters (e.g., co-adsorbates that enhance reactions) may be attracted by the electric-field to each other or specific reaction sites. In addition, desired reactions may speed up or undesirable reactions may slow down. The electric-fields may affect the temperatures at which these processes occur and may stabilize or destabilize these processes.

Surface relaxations or reconstructions may be shifted to lower (or higher) temperatures. Old relaxation/reconstruction processes may be prevented or new ones may be made available. In an embodiment, “electric field electrodes” may be used to prevent phase reconstruction by renewing the surface with, for instance, oxygen species that were lost as a result of poisoning, and subsequently resulted in new surface phases being formed.

The electric field enhancement may speed up or slow down diffusion of certain species, resulting in changes to a reaction. The collision of gas molecules from the gas phase may also be changed if the electric field has long-range effects; this may alter the way a reaction proceeds.

The electric field may result in changes to the thermodynamics of a system, which often times plays an important part in how reactions proceed. In devices or applications where the reactions depend on the thermodynamics of various species or complexes, the “electric-field electrodes” can shift the equilibrium to achieve new reactions and/or complexes, or to change the temperature at which such reactions occur.

In addition, it may be possible to affect the gas phase in such away that the processes mentioned above are altered.

Accordingly, the electric field generated with the “electric-field electrodes” can be effectively “shaped” to produce the desired field profile in the device/support or at specific locations in the device/support. Furthermore, the shaped electric field may be actively changed with time if desired.

The electric field generated with the “electric-field electrodes” may be used to purposefully (or unintentionally) “force” adsorption, desorption, or specific reactions.

The electric field generated with the “electric-field electrodes” may be used to reverse the effects of poisoning by inhibitors.

5 The electric field generated with the “electric-field electrodes” may be used to attract reaction promoters.

10 The electric field generated with the “electric-field electrodes” may be used to enhance performance in electrochemical devices, (e.g., gas sensors and fuel cells), non-electrochemical devices (e.g., gas sensors which do not utilize an electrolyte), and in general catalytic reactions (e.g., ethylene oxidation) or electrochemically-enhanced (i.e., NEMCA) reactions.

15 The electric-field electrodes may be used to improve such features as sensitivity, selectivity, and response time in a gas sensor. The “electric-field electrodes” may be incorporated into a gas sensor array, which has other performance enhancing features, such as imbedded heaters, etc. The gas sensor array may have multiple numbers of electrodes and may be used to detect a multitude of gases. The sensing electrodes in such a gas sensor array may be in the same gas environment and may, but need not, include an air-reference or other type of reference electrode.

20 In an electrochemical system, localized fields exist around a region known as the dipole layer. This region is important for the way in which electrochemical reactions occur in such systems. By using the external electric-field generated with the “electric-field electrodes”, these “natural” electric fields may be altered. Direct control of the field can result in desirable changes to the system. NEMCA can be limited in the control of the electric field that results from a direct bias, as increased direct biases can result in Joule heating and/or decomposition of the electrolyte or electrodes. However, the limit of the electric field produced with the “electric field electrodes” is likely many orders of magnitude higher.

25 “Electric-field electrodes” can be used in a gas sensor to change sensitivity, selectivity, and response time of the device. “Electric-field electrodes” can also be used to alter catalytic reactions as demonstrated by their effects on the gas composition coming off the device and species that exist at the device surface.

30 Certain embodiments of the present invention can involve potentiometric, impedancemetric (resistive and/or capacitive), or amperometric gas sensors.

Figures 1A-1C show an embodiment for applying an electric field using electric field electrodes that are parallel to the sensing electrodes of a gas sensor. Referring to Figure 1A, which shows a cross-section of the parallel-field embodiment for gas sensor applications according to an embodiment of the present invention, sensing electrodes 1 and 2 can be attached to substrate 3. The substrate 3 can be an electrolyte or other material. In a specific embodiment where the substrate 3 is formed of electrolyte, the substrate can be formed of yttria stabilized zirconia (YSZ). In one embodiment, the sensing electrodes 1 and 2 can be formed of the same material. However, in other embodiments, the sensing electrodes 1 and 2 can be formed of different materials. For example, in a specific embodiment, the first sensing electrode 1 can be formed of La_2CuO_4 , and the second sensing electrode 2 can be formed of platinum (Pt). An electrochemical cell is formed when the first electrode 1 and second electrode 2 are in contact with the substrate 3, when substrate 3 is an electrolyte

The sensing electrodes 1 and 2 can be provided in a single gas environment. On the opposite side of the solid electrolyte 3 from the first and second sensing electrodes 1 and 2, electric-field electrodes can be provided to apply a parallel electric field. A first electric-field electrode 6 and a second electric-field electrode 8 can be provided corresponding to the first sensing electrode 1. A third electric-field electrode 7 and a fourth electric-field electrode 9 can be provided corresponding to the second sensing electrode 2. In a specific embodiment, a first insulator 4 can be provided beneath the first and second electric-field electrodes 6 and 8 and the solid electrolyte 3, and a second insulator 5 can be provided between the third and fourth electric-field electrodes 7 and 9 and the solid electrolyte 3. The first and second insulators 4 and 5 can be formed of, for example, Al_2O_3 . The electrodes of the electric-field electrodes can be formed of a conductive material. For example, the electrodes can be formed of gold (Au). A cap layer can be provided on each of the electric-field electrodes for insulation and improved adhesion. The cap layers can be formed of, for example, Al_2O_3 . The insulation layers 4 and 5 can allow the conduction layers of the electric-field electrodes 6 and 7 to not make contact with substrate 3. If substrate 3 is selected to be an electrolyte, then insulation layers 4 and 5, and conduction layers 6 and 7, are not considered part of the electrochemical cell.

Figure 1B shows the top surface of the parallel-field embodiment shown in Figure 1A, with sensing electrode 1 and electrode 2 positioned on the substrate 3. Metallic leads or other metallization (not shown) can be attached to the sensing electrodes in many ways. For the

sensor application these leads can be used to transmit information about the electromotive field (EMF) at the electrode to a measurement device.

Figure 1C shows the bottom surface of the parallel-field embodiment shown in Figure 1A, with insulation layer 4 and conduction layers 6 and 8 making up two “electric-field electrodes.” Metallic leads (not shown) can be attached to the electric-field electrodes in many ways.

Different “charging schemes” may be used to get variations in the gas sensor sensitivity, selectivity, response time, etc. This is done by accumulating positive (+) or negative (-) charge via an applied voltage at any of conduction layers 6 through 9.

As shown in Table 1 below, there are a number of different “charging schemes” each one resulting in a different electric-field distribution in the device, and hence a different modification of the sensor behavior.

Table 1

#	Conduction layer 6	Conduction layer 7	Conduction layer 8	Conduction layer 9
1	+ (-) charge	floating	floating	floating
2	+ (-) charge	+ (-) charge	floating	floating
3	+ (-) charge	+ (-) charge	+ (-) charge	+ (-) charge
4	+ (-) charge	- (+) charge	+ (-) charge	- (+) charge
5	+ (-) charge	+ (-) charge	- (+) charge	- (+) charge
6	+ (-) charge	ground	floating	- (+) charge
7	Etc.	Etc.	Etc.	Etc.

As discussed herein, the electric-field electrodes may be used to “shape” the field profile in a device. This technique was tested in a gas sensor device and modeled to show how the field profile may change during “shaping.”

Figures 2A-2C show an embodiment for applying a shaped electric field to sensing electrodes of a planar gas sensor.

Referring to Figure 2A, which shows a cross-section of the shaped-field embodiment for gas sensor applications, sensing electrodes 13 and 17 can be attached to a substrate 24. The substrate 24 can be an electrolyte or other material. In a specific embodiment where the substrate 3 is formed of electrolyte, the substrate can be formed of YSZ. As described with respect to the embodiment illustrated in Figures 1A-1C, the sensing electrodes can be formed of the same or different material. For example, the first sensing electrode 13 can be formed of La_2CuO_4 and the second sensing electrode 17 can be formed of Pt. If substrate 24 is an electrolyte, then the first sensing electrode 13, second sensing electrode 17, and the substrate

24 make up an electrochemical cell. The sensing electrodes 13 and 17 can be provided in a single gas environment.

Electric-field electrodes can be provided at positions on the solid electrolyte 24 to apply an actively shaped electric field. A first electric-field electrode 11 can be provided in a ring shape around the first sensing electrode 13, and a second electric-field electrode 15 can be provided in a ring shape around the second sensing electrode 17. A third electric-field electrode 19 can be provided on the opposite side of the solid electrolyte 24 from the first sensing electrode 13 and in a ring shape corresponding to the first electric-field electrode 11, and a fourth electric-field electrode 22 can be provided on the opposite side of the solid electrolyte 24 from the second sensing electrode 17 and in a ring shape corresponding to the second electric-field electrode 15. In a specific embodiment, a first insulator 10 can be provided in a ring shape between the first electric-field electrode 11 and the solid electrolyte 24, a second insulator 14 can be provided in a ring shape between the second electric-field electrode 15 and the solid electrolyte 24, a third insulator 18 can be provided in a ring shape between the third electric-field electrode 19 and the solid electrolyte 24, and a fourth insulator 21 can be provided in a ring shape between the fourth electric-field electrode 22 and the solid electrolyte 24. The first, second, third and fourth insulators 10, 14, 18 and 21 can be formed of, for example, Al_2O_3 . The electrodes of the electric-field electrodes can be formed of a conductive material. For example, the electrodes can be formed of gold (Au).

A cap layer can be provided on each of the electric-field electrodes for insulation. In a specific embodiment, a first cap layer 12 can be provided on the first electric-field electrode 11, a second cap layer 16 can be provided on the second electric-field electrode 15, a third cap layer 20 can be provided on the third electric-field electrode 19, and a fourth cap layer 23 can be provided on the fourth electric-field electrode 22. The cap layers can be formed of, for example, Al_2O_3 . The cap layer may be omitted if desired. Metallic leads or other metallization (not shown) may be sandwiched between the individual conduction layers and cap layers. The conduction layers of the electric-field electrodes do not make contact with substrate 24, though if desired the cap layer can do so. If substrate 24 is an electrolyte, then layers 10 through 12, 14 through 16, 18 through 20, and 21 through 23 are not part of the electrochemical cell.

Figure 2B shows a top surface of the shaped-field embodiment, with sensing electrode 13 and electrode 17 attached to substrate 24. Metallic leads or other metallization (not shown) can be attached to the sensing electrodes in many ways. For the sensor application these leads

are used to transmit information about the EMF at the electrode to a measurement device. Multiple sensing electrodes and “electric-field electrodes” may be incorporated into such a device as well, making it a gas sensor array.

Figure 2C shows a bottom surface of the shaped-field embodiment, with insulation layers 10, 14, 18, and 21, and conduction layers 11, 15, 19, and 22 making up four electric-field electrodes. Metallic leads (not shown) can be attached to an “electric-field electrodes” (making contact with the conduction layers) in many ways. These electric-field electrodes may also have geometries that are different from a ring-shape; in fact the sensing (or other active material) may be formed in a ring with the electric field electrode in arranged in the center. Different “charging schemes” may be used to get variations in the gas sensor sensitivity, selectivity, response time, etc. This is done by accumulating positive (+) or negative (-) charge via an applied voltage at any of conduction layers 11, 15, 19, and 22.

As shown in Table 2 below, there are a number of different “charging schemes” each one resulting in a different electric-field distribution in the device, and hence a different modification of the sensor behavior. Charging schemes 1 through 3 were tested using the shaped-field embodiment. Note, in charging scheme 6, conduction layers 11 (and 19) and 15 (and 22) have different charge values (i.e., the voltage applied to each is of a different magnitude). The other schemes are possible but have not been tested yet; they are included to show the advantages of a “shaped field” device.

Table 2

#	Conduction layer 11	Conduction layer 15	Conduction layer 19	Conduction layer 22
1	+ (-) charge	+ (-) charge	- (+) charge	- (+) charge
2	+ (-) charge	- (+) charge	- (+) charge	+ (-) charge
3	+ (-) charge	floating	- (+) charge	floating
4	floating	+ (-) charge	Floating	- (+) charge
5	+ (-) charge	ground	floating	- (+) charge
6	ground	+ (-) charge	+ (-) charge	floating
7	+ (-) charge 1	+ (-) charge 2	- (+) charge 1	- (+) charge 2
8	Etc.	Etc.	Etc.	Etc.

Figures 3A-3H illustrate the results from the shaped-field embodiment shown in Figures 2A-2C. The sensing electrodes 13 and 17 are La_2CuO_4 and Pt, respectively.

Figure 3A represents the (potentiometric) NO sensor results from the shaped-field embodiment shown in Figures 2A-2C. The sensing electrodes are Pt and La_2CuO_4 , which

were exposed to the same gas environment (i.e., no air-reference). This plot compares the conditions with no electric field to those with a +1V bias using charging scheme 1 at 450C, 500C, 550C, and 600C. In the experiment represented in this figure, the top electric-field electrodes (surrounding the Pt and La₂CuO₄ sensing electrodes) were positively biased. The corresponding “electric-field electrodes” on the opposite side of the substrate were both negatively biased. In other words, a voltage was applied between the top field electrodes (high potential) and the bottom field electrodes (low potential).

Figure 3B represents the NO₂ sensor results from the shaped-field embodiment shown in Figures 2A-2C. The sensing electrodes are Pt and La₂CuO₄. This plot compares the conditions with no electric field to those with a +1V bias using charging scheme 1. In the experiment represented in this figure, the top electric-field electrodes (surrounding the Pt and La₂CuO₄ sensing electrodes) were positively biased. The corresponding “electric-field electrodes” on the opposite side of the substrate were both negatively biased.

Figure 3C shows the steady state sensor response of the shaped-field embodiment shown in Figures 2A-2C. In this case, charging scheme 1 (table 2) was used to apply negative (-) biases of different strength to top “electric field electrodes (surrounding the Pt and La₂CuO₄ sensing electrodes). The corresponding “electric-field electrodes” on the opposite side of the substrate were both positively biased.

Figures 3E shows the NO and NO₂ sensor response for biasing scheme 2 (Table 2) applied to the embodiment shown in Figures 2A-2C. In the cases marked as positive bias, a high potential) was applied to the electric field electrode surrounding the La₂CuO₄ sensing electrode (conduction layer 11) and at the electric field electrode on the opposite side of the substrate, aligned with the Pt sensing electrode (conduction layer 22). Simultaneously, a low potential was applied at the electric field electrode surrounding the Pt sensing electrode (conduction layer 15) and at the electric field electrode on the opposite side of the substrate, aligned with the La₂CuO₄ electrode (conduction layer 19). In cases marked as negative (-) bias, the high and low potentials applied at the electric field electrodes were reversed.

Figure 3F and 3G show the NO and NO₂ sensitivity results for biasing scheme 3 applied to the embodiment shown in Figures 2A-2C. In this case a negative bias was applied to the electric field electrodes (conduction layer 11) surrounding the La₂CuO₄ sensing electrode, with a positive bias applied to the corresponding electric field electrode on the opposite side of the substrate (conduction layer 19). The other two electric field electrodes

(conduction layers 15 and 22), aligned with the Pt sensing electrode, were left unbiased (floating).

Figure 3H shows the NO and NO₂ sensitivity results for biasing scheme 4 applied to the embodiment shown in Figures 2A-2C. In this case a positive (or negative (-)) bias was applied to the electric field electrodes (conduction layer 15) surrounding the Pt sensing electrode, with a negative (or positive) bias applied to the corresponding electric field electrode on the opposite side of the substrate (conduction layer 22). The other two electric field electrodes (conduction layers 15 and 22), aligned with the La₂CuO₄ sensing electrode, were left unbiased (floating).

The use of the electric field electrodes in the various charging schemes from Table 2 with the embodiment shown in Figures 2A-2C, resulted in different sensing behavior for the gas sensor (Figures 3A-3H). As illustrated in Figure 3A, for charging scheme 1 (Table 2), the sensor response to NO changed as the electric field bias of 1 V was applied. Furthermore, the magnitude of the changes was different as the ambient temperature varied. However, when compared to Figure 3B, it is clear that the electric-field electrodes enhanced the NO₂ response of the device by quite a bit more. The selective enhancement or reduction of the mechanisms that cause the sensor response can be very useful in a number of electrochemical devices, non-electrochemical devices, and other related processes. Charging scheme 1 (Table 2) resulted in extremely large (~20X increase in NO sensitivity and ~10X increase in NO₂ sensitivity) as shown in Figures 3C and 3D. Furthermore, the sensitivity to NO₂ starts off negative and trends towards zero sensitivity before achieving a positive response. At the same time, the NO response only becomes increasingly positive. Therefore, it is possible that NO selectivity over NO₂ can be achieved.

The use of charging scheme 2 shown in Figure 3E demonstrates the capability of a shaped electric field to further enhance a gas sensor. In this case, a positive field bias resulted in an increased NO₂ response with increased bias, with a slightly increased NO sensitivity but no additional changes as the bias increased. On the other hand, negative field biases, resulted in decreased NO sensitivity to almost zero, while maintaining NO sensitivity. In fact for the bias of -0.5 V to the electric field electrodes, the NO sensitivity was negligible while the NO₂ sensitivity actually increased.

As shown in Figure 3F-3G, charging scheme 3 (Table 2) resulted in similar changes in both NO and NO₂ sensitivity as the electric field bias was changed. This suggests that this charging scheme might be used for achieving an enhanced total-NO_x sensor signal.

Figure 3H further demonstrates the ability of the various shaped electric fields to enhance a device in a number of ways. In this case, the results indicate that the bias scheme may result in NO selectivity because the NO₂ sensitivity trends toward zero while the NO sensitivity remains relatively unchanged. Furthermore, the fact that different results were achieved for each shaped field bias schemes suggests that similar enhancements can be used to improve other electrochemical devices, non-electrochemical devices, and other related processes.

Figure 4A is a representation of the electric-field contour map 25 showing relative field strengths for the shaped-field embodiment of Figures 2A-2C using charging scheme 3. Here, “electric-field electrode” 26 has a positive charge, while “electric-field electrode” 28 has a negative charge of equal magnitude. “Electric-field electrodes” 27 and 29 are left floating. Each contour 25 in the figure represents different field strengths moving away from the device surface and throughout the gas environment surrounding the device. While not shown, it should be noted that the field contours also extend through substrate 30 and other parts of device (i.e., the field penetrates the device).

Figure 4B is a representation of the electric-field vector map 31 for the same charging scheme as was presented in Figure 4A. Each arrow in the figure represents the direction of the electric field in space. The electric field moves from regions of positive to negative charge. Looking at Figure 4B and referring to Figure 2B, it is clear that for this charging scheme (in the ideal case) the electric field is uniform near the center of the rings making up “electric-field electrodes” 26 and 28. However, the field is non-uniform near center of the rings for “electric-field electrodes” 27 and 29. The electric field contour map and electric field vector map in Figures 4A and 4B, will change depending on the values of several parameters (e.g., the voltage at the “electric-field electrodes” and/or the charging scheme used). While not shown, it should be noted that the field vectors also extend through substrate 30 and other parts of device (i.e., the field penetrates the device). Also, note that fringing effects near the edges of the “electric-field” electrodes have not been considered in the ideal case.

Figure 4C is a representation of the electric-field vector map 32 for charging scheme 1 of the shaped-field embodiment in Figures 2A-2C. Here, “electric-field electrodes” 33 and 34 have a positive charge, while “electric-field electrodes” 35 and 36 have a negative charge. Looking at Figure 4C and referring to Figure 2C, it is clear that for this charging scheme (in the ideal case) the electric field is uniform near the center of the rings making up “electric-

field electrodes” 33, 34, 35 and 36. Furthermore, the direction of the field vectors through the middle of the rings is the same for the left pair of rings (33 and 35) as it is for the right pair of rings (34 and 36). This is also the same direction as between the two pairs of rings (i.e., through the very middle of the device, perpendicular to the surface). Also note that the field distribution in this scheme is symmetric about the device and surrounding gas environment (assuming ideal case and no interference from neighboring objects). This electric field vector map will change depending on the values of the voltage at the “electric-field electrodes” (and if the charging scheme changes). While not shown, it should be noted that the field vectors also extend through substrate 37 and other parts of device (i.e., the field penetrates the device).

Figure 4D is a representation of the electric-field vector map 38 for charging scheme 2 of the shaped-field embodiment in Figures 2A-2C. Here, “electric-field electrodes” 39 and 42 have a positive charge, while “electric-field electrodes” 40 and 41 have a negative charge. Looking at Figure 4D and referring to Figure 2C, it is clear that for this charging scheme (in the ideal case) the electric field is uniform near the center of the rings making up “electric-field electrodes” 39, 40, 41 and 42. Furthermore, the field vector direction through the middle of the rings is NOT the same for the left pair of rings (39 and 41) as it is for the right pair of rings (40 and 42); the directions are opposite each other (and perpendicular to the surface). Also note that the field distribution in this scheme is symmetric about the device and surrounding gas environment (assuming ideal case and no interference from neighboring objects). While this latter fact, mirrors the situation displayed in Figure 4C, the field in between the two pairs of rings (i.e., at the very middle of the device) is no longer perpendicular to the surface; rather the field is now parallel to the surface. This electric field vector map will change depending on the values of the voltage at the “electric-field electrodes” (and if the charging scheme changes). While not shown, it should be noted that the field vectors also extend through substrate 43 and other parts of device (i.e., the field penetrates the device). Also, in addition to differences in the field vector map between charging schemes 2 (Figure 4D) and 1 (Figure 4C), it is worth noting that the field strength represented by the contour map for these two instances have also changed (not shown).

Figures 4A-4D are simple 2D models mainly to represent the idea that different charging schemes (and embodiments) can allow the electric-field enhancement to be (actively) fine tuned in a device or general catalysis process. The field distribution, etc. may be different in a real device or process because the presence of the sensing electrodes and

other components will also contribute to the field, making it different from the simple cases shown. The electrostatic and chemical interaction with the device, catalyst, gas, adsorbates, etc. will depend on these field contour and vector maps. Therefore, these interactions can be (actively) fine tuned depending on the device or general catalysis process for a given application.

Figure 5A represents a sensor embodiment utilizing an air-reference electrode 51. This embodiment was used to show that catalytic reactions are changing during use of the electric field electrodes, as exhibited by alteration of the measured gas composition. Insulation layers 45 and 48, conduction layers 46 and 49, and cap layers 47 and 50 making up four “electric-field electrodes.” Sensing electrode 44 and air-reference electrode 51 are attached to substrate (electrolyte or other material) 52.

Figure 5B shows a top surface of the air-reference sample with “electric-field electrodes” embodiment, with cap layer 47 shown. Metallic leads or other metallization (not shown) can be attached to the sensing or air-reference electrodes in many ways. For the sensor application these leads are used to transmit information about the EMF at the electrode to a measurement device. Multiple sensing electrodes and “electric-field electrodes” may be incorporated into such a device as well, making it a gas sensor array.

Figure 5C shows a bottom surface of the air-reference sample with “electric-field electrodes” embodiment. Air-reference electrode 51 is attached to substrate 52, and surrounded by the “electric-field electrode on this surface. From this viewpoint, the cap layer 50 is visible.

This sensor device includes a first, rectangular ring-shaped “electric-field electrode” on one side of an electrolyte. In the middle this rings, a Pt air-reference electrode was deposited. On the opposite side, a La_2CuO_4 electrode was attached to the electrolyte. On top of this electrode was a second, plate-shaped “electric-field electrode”. The La_2CuO_4 electrode and second field electrode were exposed to the active gas stream, while the Pt air-reference and first field electrode remained at constant oxygen partial pressure (i.e., air).

The sensor was evaluated for multiple NO_x concentrations in 3% O_2 under an “electric-field electrode” bias of 0, 2, 5, and 8 V in the positive (high potential on La_2CuO_4 side) and negative (high potential on Pt side) directions. These tests were performed at temperatures of 450°C, 500°C, and 550°C and repeated twice for each condition. The sensors under the influence of the electric field were compared to the unbiased device at each temperature. The sensor signals were very low at 550C and 500C, which resulted in little or

no change in sensitivity with applied field (not shown), except for the - 8 V setpoint with NO at 500C. However, as seen in Figure 6A and 6B, at all temperatures, alteration of the field bias produced changes in the gas composition coming off the La₂CuO₄ sensing electrode as detected with mass spectrometry. These plots were made using the measured NO_x compositions from the 650 ppm NO or NO₂ feed composition of the respective gas steps. These plots are in terms of electric-field bias voltage because of the difficulty in ensuring the modeled field- strengths accurately represent reality when applied to handmade samples. As evident from both plots in Figure 4, there were major changes in NO_x levels for both NO and NO₂ gas steps. Furthermore, in the case of the NO₂ gas steps, a shoulder/peak evolves in the measured NO₂ curves (around - 5 V field bias) as temperature increases.

At 450°C, there were significant changes for both NO and NO₂ sensitivity as the electric field was created on the device. The sensitivity (mV/decade ppm NO_x) to gas steps and concentrations measured during the 650 ppm NO or NO₂ feed composition can be seen in Figures 6C and 6D. In the case of NO gas steps, from region I to II a decreasing (+) field bias resulted in concurrent increases of NO and NO₂ concentrations without much change in sensitivity. In region II, a transition from (+) to (-) field bias occurred with the result of a sharp decrease in measured NO and a more gradual decrease in NO₂. This difference in the change of species concentrations appears to have caused the sensitivity to decrease in going from region II to III. With a further decrease in the now (-) field bias there resulted a continuing decrease in NO₂ levels with essentially no change in NO. This was accompanied with a dramatic increase in the NO sensitivity of the device. Finally in transition from region III to IV, there was a relatively large decrease in sensitivity as the NO and NO₂ concentrations dropped in response to a more (-) field bias.

Now considering the four regions of inflection in Figure 5 for NO₂ gas steps at 450°C, there appear to have been more complicated changes to the sensing mechanism. In going from region I to II, there was a sharp increase in the NO₂ concentration accompanied with a slower decrease in NO. This resulted in a sharp shift in the NO₂ sensitivity to smaller, more positive values. In the middle of region II, there was a crossover of the NO and NO₂ concentrations with a concomitant dip in NO₂ sensitivity. After a small increase at the more (-) end of region II, there was a sharp decrease in NO₂ sensitivity as region III begins. Also during this transition was a second crossover of the NO and NO₂ concentrations as the amount of NO₂ decreased sharply and NO more slowly increased. As region III nears region

IV, the measured NO concentration began to inflect and decreased while the NO₂ continued to decrease. As a result, the NO₂ sensitivity increased slightly in region IV.

The results from the embodiment in Figures 5A-5C, as shown in Figures 6A-6D demonstrate that use of the electric field electrodes can change the catalytic properties of a material, which may be used in an electrochemical device, non-electrochemical device, or other related (catalytic) processes. Furthermore, these results can enhance a gas sensor by causing large changes in sensitivity to various gas species.

The sample shown in Figure 7A was used in the field-assisted desorption measurements shown in Fig. 7B through 7E. These results demonstrated that an indirectly applied electric field can affect the behavior of NO_x on the surface of La₂CuO₄ even at relatively small field strengths. Temperature Programmed Desorption (TPD) experiments were conducted on a sample with “electric-field electrodes” as shown in Figure 7A. This sample included a section of a porous La₂CuO₄ bar 53 with insulating layer 54 and 55 (Al₂O₃) and conducting layers 56 and 57 an(Au) attached to either end. Though not shown, an effect was also seen on a high-surface area powder sample of La₂CuO₄. During several sets of experiments, the sample was biased at the conduction layers 56 and 57 with various applied voltages.

TPD is an experimental technique in which initial quantities of a gas are adsorbed at relatively low temperatures (e.g., 300C) and then cooled to room temperature. The gas of interest is then shut off, and an inert gas such as helium is flowed through the reactor. The temperature is then ramped at high linear rate (e.g., 30°C/min) as the evolution of desorbed species is monitored with a mass spectrometer.

As the electric-field voltage setpoint increased, the desorption peaks for NO (Figure 7B) shifted to higher temperatures, while maintaining similar initial peak shapes, albeit different intensities. In addition to the upward temperature shift of the peaks, the lingering desorption of NO at high temperatures was expressed as more defined peaks. This shift was accompanied by the appearance of substantial NO₂ desorption peaks at the same temperatures as NO desorption (Figure 7C. Changes in peak intensity and area indicate that the adsorption/desorption energies and chemisorption mechanisms are likely changing as a result of the electric-field. The quantity of gases desorbed from the sample can be found in Table 3.

Table 3
NO Adsorption

TABLE 3. Total amount NO_x adsorbed during NO + O₂ TPD.

E-field Bias Voltage	Total μmol NO Adsorbed	Total μmol NO₂ Adsorbed	Total μmol NO_x Adsorbed
0 V	13.080	7.848	20.868
2 V	13.450	5.165	18.615
5 V	6.706	8.591	15.297
8 V	11.040	4.994	16.034

5

Identical experiments were performed for NO₂ adsorption (Figures 7D and 7E). In these results, there were less pronounced shifts in the desorption energies, but definitive changes in the intensities of the various peaks indicates possible changes in chemisorption mechanisms. Desorption amounts can be seen in Table 4.

10

Table 4
NO₂ Adsorption

TABLE 4. Total amount NO_x adsorbed during NO₂ + O₂ TPD.

E-field Bias Voltage	Total μmol NO Adsorbed	Total μmol NO₂ Adsorbed	Total μmol NO_x Adsorbed
0 V	15.220	13.240	28.460
2 V	14.550	11.470	26.020
5 V	13.290	10.380	23.670
8 V	14.000	9.105	23.105

15

The results from the

Sensor embodiments in accordance with the subject invention can utilize potentiometric, impedancemetric, and/or amperometric measurements. The sensors can locate all of the electrodes in the same gas environment and can use an air reference or some other type of reference.

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In various embodiments, the voltage(s) applied to the “electric-field electrodes” may be alternatively supplied with a potentiostat or other device that keeps the charge at the “electric-field electrodes” equal to the desired value. In this way if the gas environment (or some phenomena) causes the charge to change, the potentiostat or other device can counteract to ensure the charge returns to the desired value. The charge may be calculated from a measured current change with time as, at least in the ideal case, there is no electronic current flowing through the device as a result of the applied voltage to the “electric-field electrodes”.

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This current measured in the “circuit” occurs as a result of changes in the accumulated charge at the insulating layer, which is only a perfect insulator in the ideal case.

Figures 8A-8H represent some of the other various configurations in which the electric-field enhancements may be used. Figure 8A shows a top view of a substrate 58 (electrolyte or other material), with each sensing electrode 59, 60, and 61 surrounded by several “electric-field electrodes” 62, 63, and 64 forming a dashed ring shape around the sensing electrodes. In Figures 8A-8H, the electric-field electrodes are shown as one body, consisting of at least an insulating layer and conducting layer and possibly a cap layer as was shown in the embodiment of Figure 2A-2C. Figure 8B shows the cross-section of 8A, with the sensing electrodes 59, 60, and 61 and “electric-field electrodes” 62, 63, and 64 displayed on one surface and heater structures 65, 66, and 67 (serpentine or other pattern) on a second surface. Figure 8C shows the cross-section of 8A, but now with the “electric field electrodes” 62, 63, and 64 and heater structures 65, 66, and 67 embedded within the substrate 58. Furthermore, there is a new layer 68 (electrolyte or other material) between the substrate 58 and sensing electrodes 59, 60, and 61.

Figures 8D and 8E show cross-sections of 8A, with heater structures 65, 66, and 67 embedded in the substrate and second layer 68 between substrate 58 and sensing electrodes 59, 60, and 61; the electric-field electrodes 70, 71, and 72 now have the form of plate-like shapes rather than the dashed arrangement seen in 8A. Furthermore, 8D shows a structure 69 that creates a cavity above each sensing electrode 59, 60, and 61; the electric field electrodes 70, 71, and 72 are attached to the inner side of this structure. Figure 8E shows a similar cavity creating structure 69, but with the electric field electrodes 70, 71, and 72 on the top surface of this structure.

Figures 8F-8H show several additional configurations of devices utilizing the electric-field enhancements. 8F shows the top view of the embodiment with two rectangular layers 80 and 81 (electrolyte or other material) on top of the substrate 73 (electrolyte or other material) containing at least two sensing electrodes 76, 77, 78, and 79 each. Layers 80 and 81 serve to separate the sensing electrodes 76, 77, 78, and 79 from the substrate 73. Structures 74 and 75 surround each of these rectangular layers and represent several electric field electrodes in a dashed arrangement. 8G represents a cross-section of 8F, showing rectangular layers 80 and 81 and corresponding sensing electrodes 76, 77, 78, and 79. Also shown are electric-field electrodes 74 and 75, and heating structures 82 and 83 on the bottom surface. Figure 8H shows another possible embodiment where one of the rectangular layers

(80 in 8F) with sensing electrodes (76 and 77 in 8F) are replaced with a gas sensitive material 84 (e.g., electrical resistance changes upon gas exposure) in contact with the substrate 73. Electrical contacts 85 and 86 are made to this material in two places. The remainder of this embodiment is the same as in 8G.

5 In a fuel cell (e.g., SOFC) oxygen is dissociation on the cathode and fuel dissociation and reactions at the anode. As discussed herein, the presence of an electric field can stabilize/destabilize adsorbate complexes on a surface. This may result in alterations to the kinetics or reaction mechanisms that will improve the performance of a fuel cell (e.g., enhance power density output). Furthermore, as discussed, removal or prevention of the
10 buildup of poisons from the fuel cell surface, particularly at the fuel side can be accomplished in accordance with embodiments of the invention using “electric-field electrodes”. The use of “electric-field electrodes” with SOFC can lower the operating temperatures and allow the use of cheaper materials in the fuel cells. Furthermore, the electric-electrodes may be used to modify the device for enhanced or maintained performance when load conditions change.

15 Figure 9A represents an electric-field enhanced, electrochemical cell (e.g., fuel cell) embodiment. Here, substrate 94, which may be an electrolyte, has an attached anode (88 or 95) and cathode (95 or 88). In other embodiments, other materials serve as the support or other support material, such as an anode support, with the electrolyte and other corresponding layers on top. Different arrangements can be used where the device is anode supported, and
20 the electrolyte is a very thin layer attached to the support. The cathode can then be deposited on top of the electrolyte, completing the cell. The “electric-field electrodes” are made up of insulation layers 88 and 91, conduction layers 89 and 92, and cap layers 90 and 93. Metallic leads, or other interconnections (not shown), may be attached to the electrodes in many different ways. This arrangement also may be formed into a stack made up of multiple cells.

25 Figure 9B is one surface of the electrochemical cell (e.g., fuel cell) embodiment. Here, cap layers 91 and 93 are visible. Electrode 87 may be the anode or cathode and is attached to substrate 95. Figure 9C is another surface of the fuel cell embodiment. Here only electrode 95 is visible. It is attached to substrate 94 and may be the anode or cathode.

Figures 10A-10C show a different electric-field enhanced, electrochemical device
30 (e.g., fuel cell) embodiment in a planar configuration. Shown is a stack configuration which may consist of any number of cells. In Figure 10A, several electric field electrodes exist, consisting of conducting layers 97, 102, and 109 insulating layers 96, 98, 101, 103, 108, and 110. In this configuration, the distinction between insulating layers and cap layers is

insignificant. These layers are deposited on substrates 99 and 111, which have various electrodes 100, 104, 105, and 107 (anodes and cathodes) attached. Though not necessary, in some cases the electric field electrodes have the added benefit of acting as seals to separate gases between the various electrochemical cells. Figure 10B shows the top surface of the embodiment in Figure 10A with substrate 99, electrode 100 (anode or cathode), and insulating layer 98 of an electric field electrode. Figure 10C shows the bottom surface of the embodiment in Figure 10A with substrate 111, electrode 106 (anode or cathode), and insulating layer 110 of an electric field electrode.

NEMCA can greatly enhance catalytic reaction rates. In the case of NEMCA, the electric field created by the applied potential or (electronic) current to the cell electrodes is limited due to the fact that increased potential (and thus field strengths) can result in permanent damage of the device. However, use of the “electric-field electrodes” can enhance the NEMCA electric field. Furthermore, the “electric-field electrodes” can have more control over adsorption and reactions than NEMCA because they may be located anywhere on the device.

As discussed herein, catalytic reactions may be altered with the use of electric fields. The “electric-field electrodes” may be incorporated into a catalyst support and thereby alter reaction pathways in a desirable way. Improvements include increased conversion yield and/or lower temperature requirements for reactions. This can result in lower costs and improved profitability for catalytic reactions.

Figure 11A represents a cross-section of catalyst bed embodiment used in catalysis processes. Metal core 112 is embedded through the middle of honeycomb 114. Outer electrode 113 is attached to the perimeter of honeycomb 114. The honeycomb pattern also may be another related shape, whose purpose is to hold catalyst particles 115. This embodiment is a polygonal-cylinder, and a voltage is applied between metal core 112 and outer electrode 113 to create an electric field around the catalyst particles which are dispersed throughout the honeycomb 114 structure. The reactant gas is flowed through the honeycomb 114 structure, where it can react on the catalyst particles. Note that the honeycomb 114 structure can also be made from an electrolyte material. In this case, an insulation layer is placed between the metal core 112 and the honeycomb 114. An insulation layer is also placed between the outer electrode 113 and the honeycomb 114 structure. Furthermore, an embodiment such as this with an electrolyte honeycomb 79 structure can be operated in an electric-field enhanced mode.

Figure 11B represents a top view of the polygonal-cylinder shape, with metal core 77 and outer electrode 78 shown. The honeycomb 79 structure is also shown. Figure 11C represents a cluster of catalyst particles 80 that could be dispersed throughout the honeycomb structure seen in Figures 11A and 11B.

5 In all embodiments shown and any others utilizing the electric field electrodes, when an electrochemical cell is involved, a combined NEMCA effect (direct bias) and electric-field enhancements (provided by the "electric-field electrodes") can improve the catalysis as discussed elsewhere. Also, multiple "electric-field electrodes" may be used in such configurations or related embodiment.

THE EMBODIMENTS OF THE INVENTION FOR WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A fuel cell, comprising:
 - an electrolyte;
 - a first electrode, wherein the first electrode is in electrical contact with the electrolyte;
 - a second electrode, wherein the second electrode is in electrical contact with the electrolyte; and
 - an electric field source,
 - wherein the electric field source creates an electric field profile proximate one or both of the first electrode and the second electrode,
 - wherein an output EMF is produced between the first electrode and the second electrode when the one or both of the first electrode and second electrode are exposed to one or more gases,
 - wherein the electric field profile proximate the one or both of the first electrode and the second electrode modifies the output EMF.
2. The fuel cell according to claim 1, further comprising:
 - a substrate, wherein the substrate comprises the electrolyte, wherein the first electrode and the second electrode are positioned on the substrate.
3. The fuel cell according to claim 1, further comprising:
 - a load connected to the first electrode and the second electrode, wherein power is delivered to the load.
4. The fuel cell according to claim 2,
 - wherein the first electrode and the second electrode are on opposite sides of the substrate,
 - wherein a first gas is in contact with the first electrode, wherein the first gas reacts such that an ion of a component of the first gas and/or an ion of the first gas travels through the

electrolyte to the second electrode and becomes the component of the first gas and/or the first gas, respectively.

5. The fuel cell according to claim 3, further comprising:

a voltage source, wherein the voltage source is configured to apply a bias across the first electrode and the second electrode.

6. The fuel cell according to claim 3, further comprising:

a current source, wherein the current source is configured to apply a bias across the first electrode and the second electrode.

7. A device, comprising:

a substrate, wherein the substrate comprises an electrolyte,

at least two electrodes positioned on the substrate, wherein the at least two electrodes are in electrical contact with the electrolyte, and

a means for creating an electric field proximate one or more of the at least two electrodes, wherein an output EMF is produced between the at least two electrodes when the one or more of at least two electrodes are exposed to one or more gases, wherein the electric field proximate the one or more of the at least two electrodes modifies the output EMF.

8. The device according to claim 7, further comprising a load connected to the two of the at least two electrode, wherein power is delivered to the load.

9. The device according to claim 7, wherein the two of the at least two electrodes are on opposite sides of the substrate, wherein a first gas is in contact with a first of the two electrodes, wherein the first gas reacts such that an ion of a component of the first gas and/or an ion of the first gas travels through the electrolyte to a second of the two electrodes and becomes the component of the first gas and/or the first gas, respectively.

10. The device according to claim 9, further comprising a means for applying a bias across the two of the at least two electrodes.

11. The device according to claim 10, wherein the means for applying the bias is a voltage source.

12. The device according to claim 10, wherein the means for applying the bias is a current source.

13. A method, comprising:
providing an electrolyte;
providing a first electrode, wherein the first electrode is in electrical contact with the electrolyte;
providing a second electrode, wherein the second electrode is in electrical contact with the electrolyte;
providing an electric field source; and
creating an electric field proximate one or more of the first electrode and the second electrode;
wherein an output EMF is produced between the first electrode and the second electrode when the one or more of the first electrode and the second electrode are exposed to one or more gases,
wherein the electric field proximate the one or more of the first electrode and the second electrode modifies the output EMF.

14. The method according to claim 13, further comprising:
providing a substrate,
wherein the substrate comprises the electrolyte, and
wherein the first electrode and the second electrode are positioned on the substrate.

15. The method according to claim 13, further comprising:
connecting a load to the first electrode and the second electrode,

wherein power is delivered to the load.

16. The method according to claim 13,
wherein the first electrode and the second electrode are on opposite sides of the substrate,
wherein a first gas is in contact with the first electrode,
wherein the first gas reacts such that an ion of a component of the first gas and/or an ion of the first gas travels through the electrolyte to the second electrode and becomes the component of the first gas and/or the first gas, respectively.

17. The method according to claim 16, further comprising:
applying a bias across the first electrode and the second electrode.

18. The method according to claim 17,
wherein applying the bias is accomplished via a voltage source.

19. The method according to claim 17,
wherein applying the bias is accomplished via a current source.

20. A method, comprising:

providing a substrate, wherein the substrate comprises an electrolyte;

providing at least two electrodes positioned on the substrate, wherein the at least two electrodes are in electrical contact with the electrolyte; and

creating an electric field proximate one or more of the at least two electrodes,

wherein an output EMF is produced between two of the at least two electrodes when the one or more of the at least two electrodes are exposed to one or more gases that react with the one or more of the at least two electrodes, wherein the electric field proximate the one or more of the at least two electrodes modifies the output EMF.

21. The method according to claim 20, further comprising: connecting a load to the two of the at least two electrode, wherein power is delivered to the load.

22. The method according to claim 20, wherein the two of the at least two electrodes are on opposite sides of the substrate, wherein a first gas is in contact with a first of the two electrodes, wherein the first gas reacts such that an ion of a component of the first gas and/or an ion of the first gas travels through the electrolyte to a second of the two electrodes and becomes the component of the first gas and/or the first gas, respectively.

23. The method according to claim 22, further comprising: applying a bias across the two of the at least two electrodes.

24. The method according to claim 23, wherein applying the bias is accomplished via a voltage source.

25. The method according to claim 23, wherein applying the bias is accomplished via a current source.

26. A catalysis device, comprising:
a substrate, wherein the substrate comprises an electrolyte;
at least two electrodes, wherein the at least two electrodes are in electrical contact with the electrolyte; and
an electric field source,
wherein the electric field source creates an electric field profile proximate a corresponding one or more surfaces of the one or more electrodes of the at least two electrodes,
wherein when the one or more surfaces of the one or more electrodes are exposed to at least one gas, creating the electric field profile modifies a catalysis reaction between the at least one gas and the one or more surfaces of the one or more electrodes.

27. The catalysis device according to claim 26,
wherein creating the electric field profile enhances the catalysis reaction between the at least one gas and the one or more surface of the one or more electrodes.

28. The catalysis device according to claim 26,
wherein when the electrolyte is exposed to the at least one gas, creating the electric field profile modifies a catalysis reaction between the at least one gas and the electrolyte.

29. The catalysis device according to claim 28,
wherein when the electrolyte is exposed to the at least one gas, creating the electric field profile enhances the catalysis reaction between the at least one gas and the electrolyte.

30. The catalysis device according to claim 26, further comprising:
a voltage source, wherein the voltage source is configured to apply a bias across two of the at least two electrodes.

31. The catalysis device according to claim 26, further comprising:
a current source, wherein the current source is configured to apply a bias across two of the at least two electrodes.

32. The catalysis device according to claim 26,
wherein the substrate comprises a porous structure that allows the at least one gas to flow through at least a portion of the porous structure, and
wherein the at least two electrodes comprise a plurality of particles within the porous structure.

33. A catalysis device, comprising:
a substrate, wherein the substrate comprises an electrolyte;
at least two electrodes, wherein the at least two electrodes are in electrical contact with the electrolyte; and
a means for exposing a surface of one or more of the at least two electrodes to one or more gases, a means for producing an electric field proximate the surface, wherein the electric

field modifies a catalysis reaction between the one or more gases and the one or more of the at least two electrodes.

34. The catalysis device according to claim 33, wherein the electric field enhances the catalysis reaction between the one or more gases and the one or more of the at least two electrodes.

35. The catalysis device according to claim 33, further comprising a means for exposing the electrolyte to the one or more gases, wherein the electric field modifies a catalysis reaction between the one or more gases and the electrolyte.

36. The catalysis device according to claim 34, further comprising a means for exposing the electrolyte to the one or more gases, wherein the electric field modifies a catalysis reaction between the one or more gases and the electrolyte.

37. The catalysis device according to claim 34, further comprising: a means for applying a bias across two of the at least two electrodes.

38. The catalysis device according to claim 37, wherein the means for applying the bias is a voltage source.

39. The catalysis device according to claim 37, wherein the means for applying the bias is a current source.

40. The catalysis device according to claim 33, wherein the substrate comprises a porous structure that allows the one or more gases to flow through, wherein the at least two electrodes comprise a plurality of particles within the porous structure.

41. A method of modifying a catalysis reaction, comprising:
providing a substrate, wherein the substrate comprises an electrolyte;
providing at least two electrodes, wherein the at least two electrodes are in contact with the electrolyte;
exposing a corresponding one or more surfaces of one or more of the at least two

electrodes to at least one gas; and

producing an electric field proximate the one or more surfaces of the one or more of the at least two electrodes, wherein the electric field modifies a catalysis reaction between the at least one gas and the one or more of the one or more of the at least two electrodes.

42. The method according to claim 41, wherein the electric field enhances the catalysis reaction between the at least one gas and the one or more of the at least two electrodes.

43. The method according to claim 42, further comprising:
exposing the electrolyte to the at least one gas, wherein the electric field enhances a catalysis reaction between at least one gas and the electrolyte.

44. The method according to claim 41, further comprising:
exposing the electrolyte to the at least one gas, wherein the electric field modifies a catalysis reaction between at least one gas and the electrolyte.

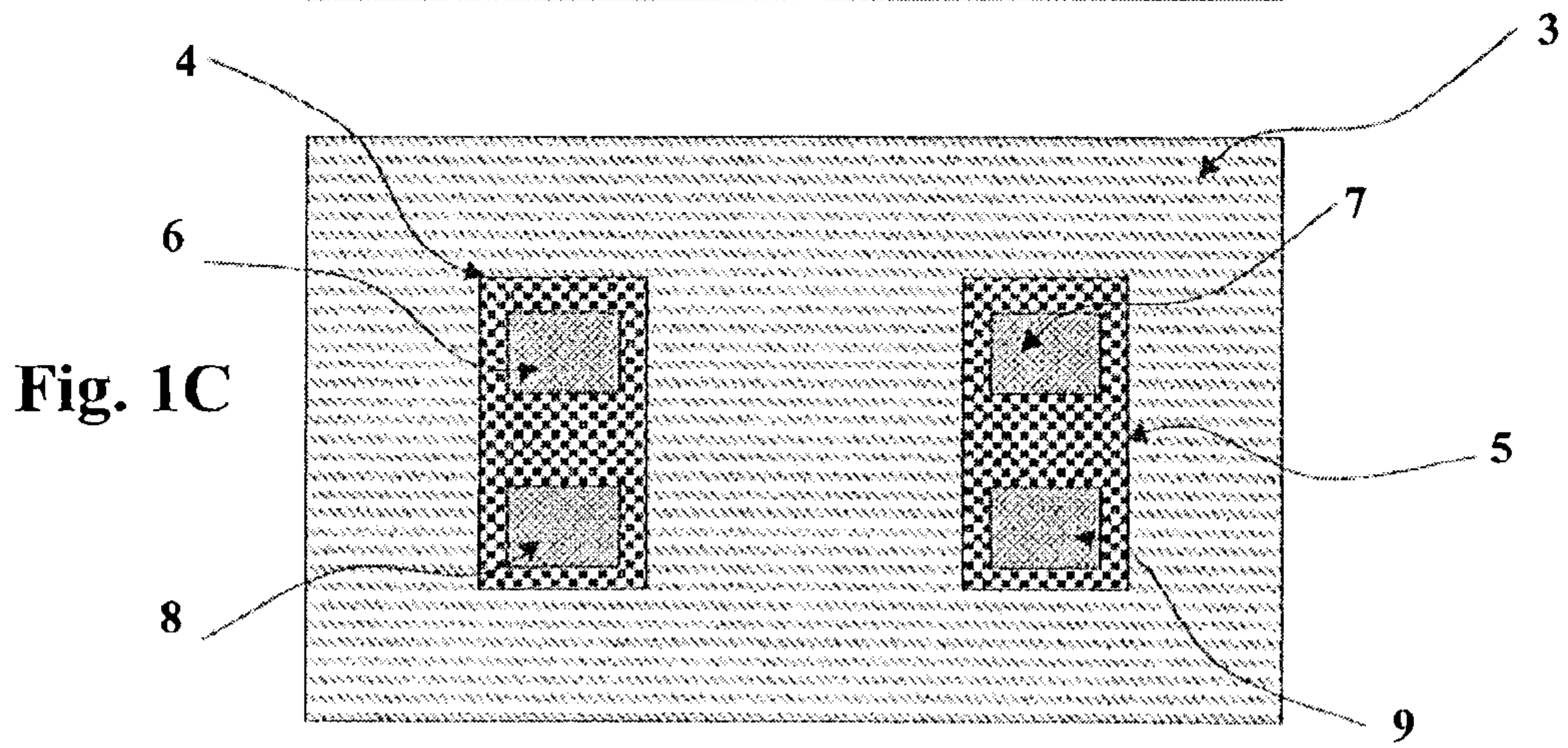
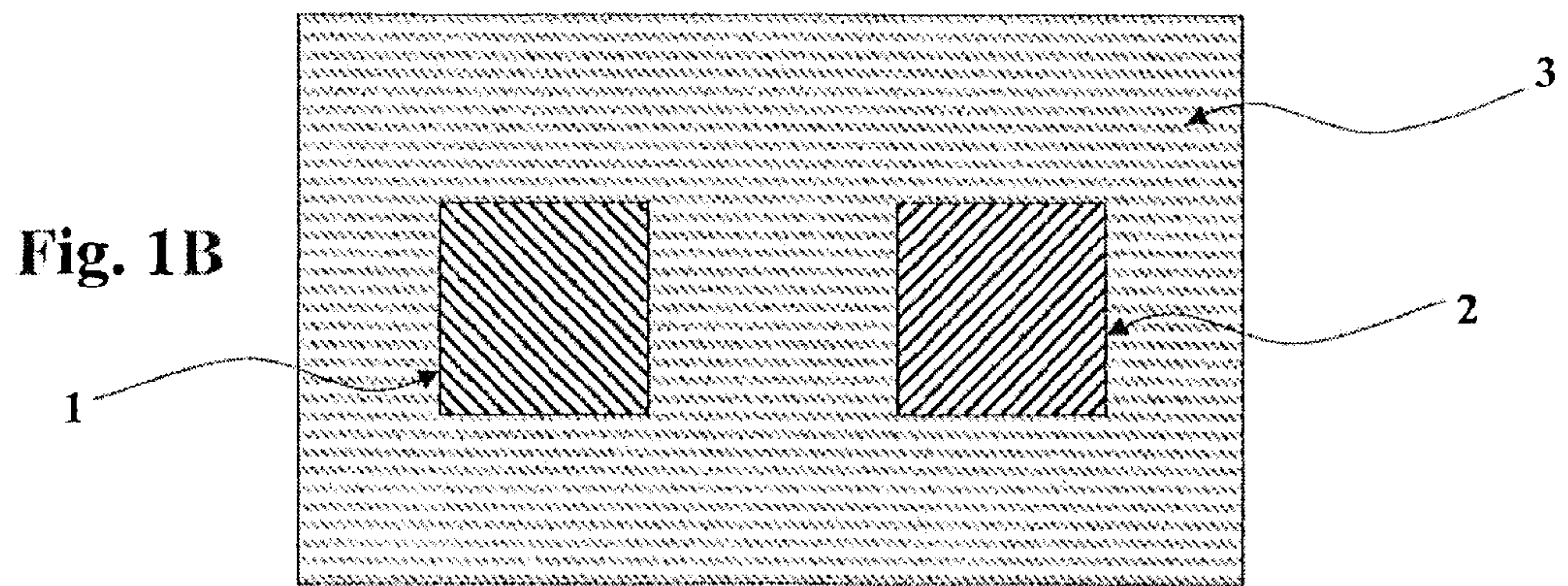
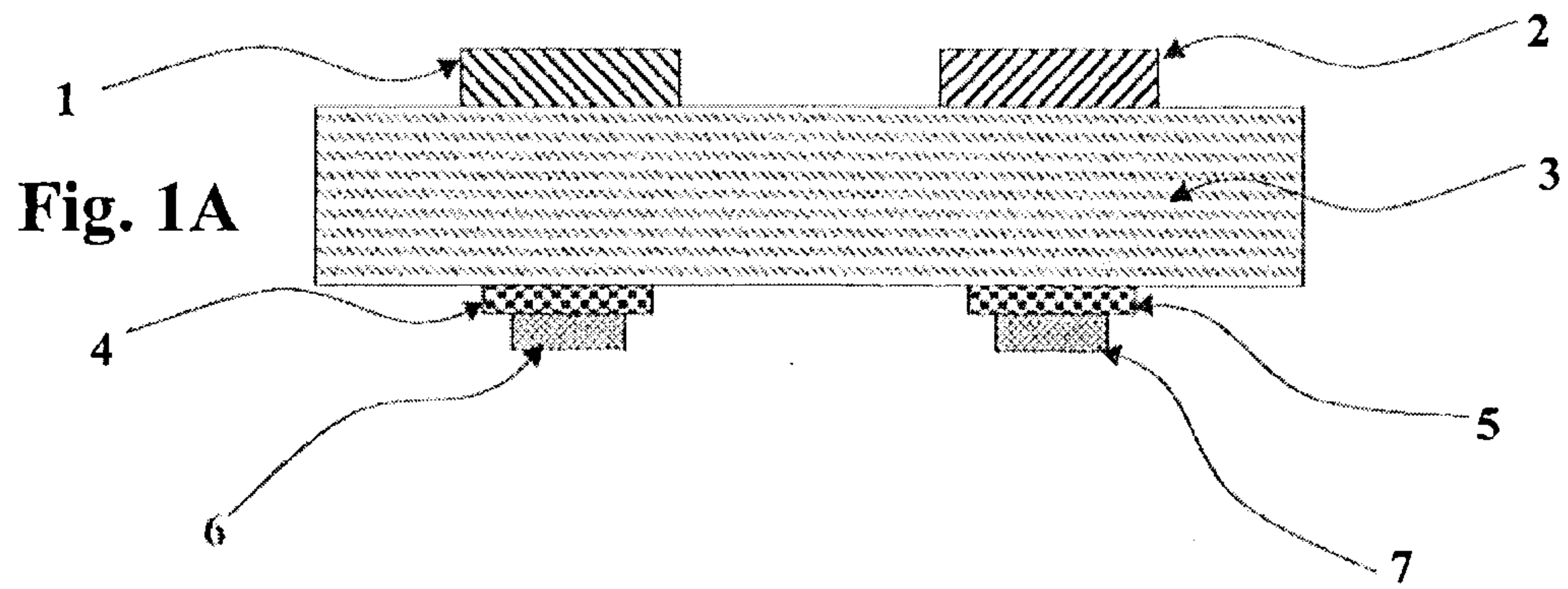
45. The method according to claim 42, further comprising:
applying a bias across two of the at least two electrodes.

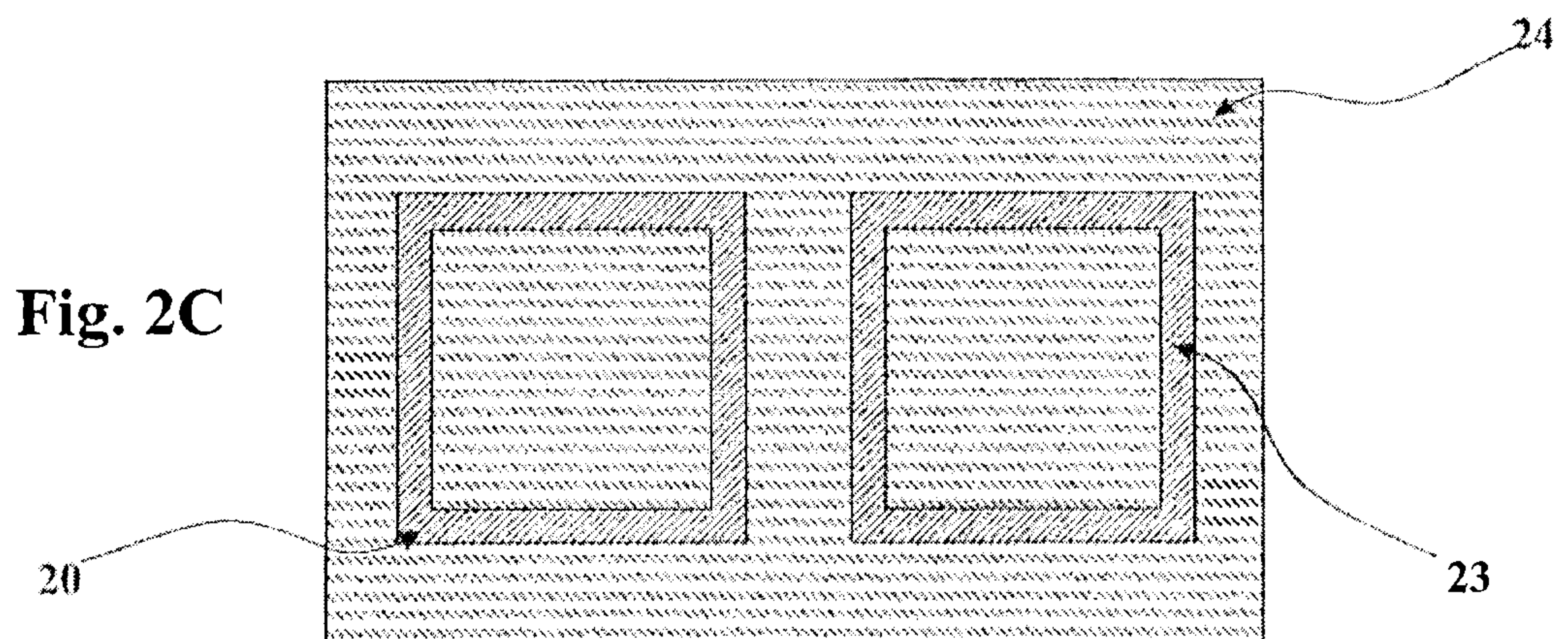
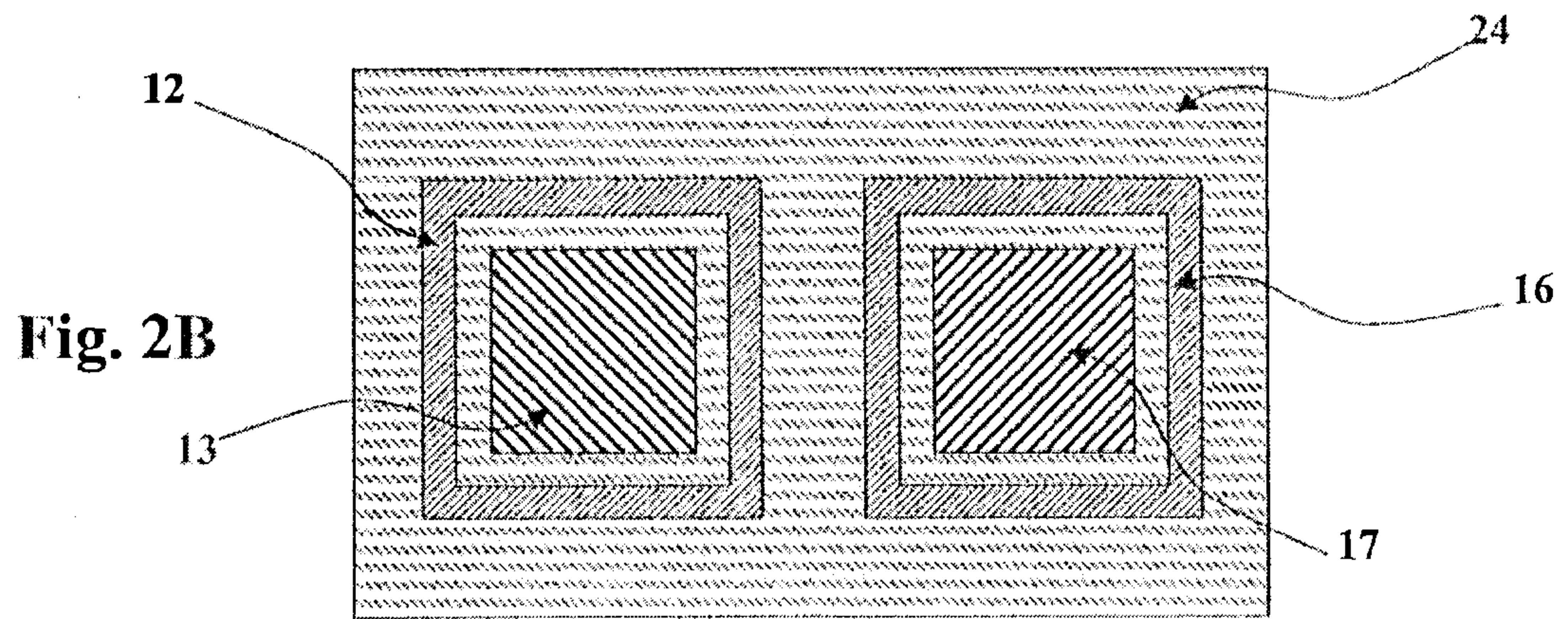
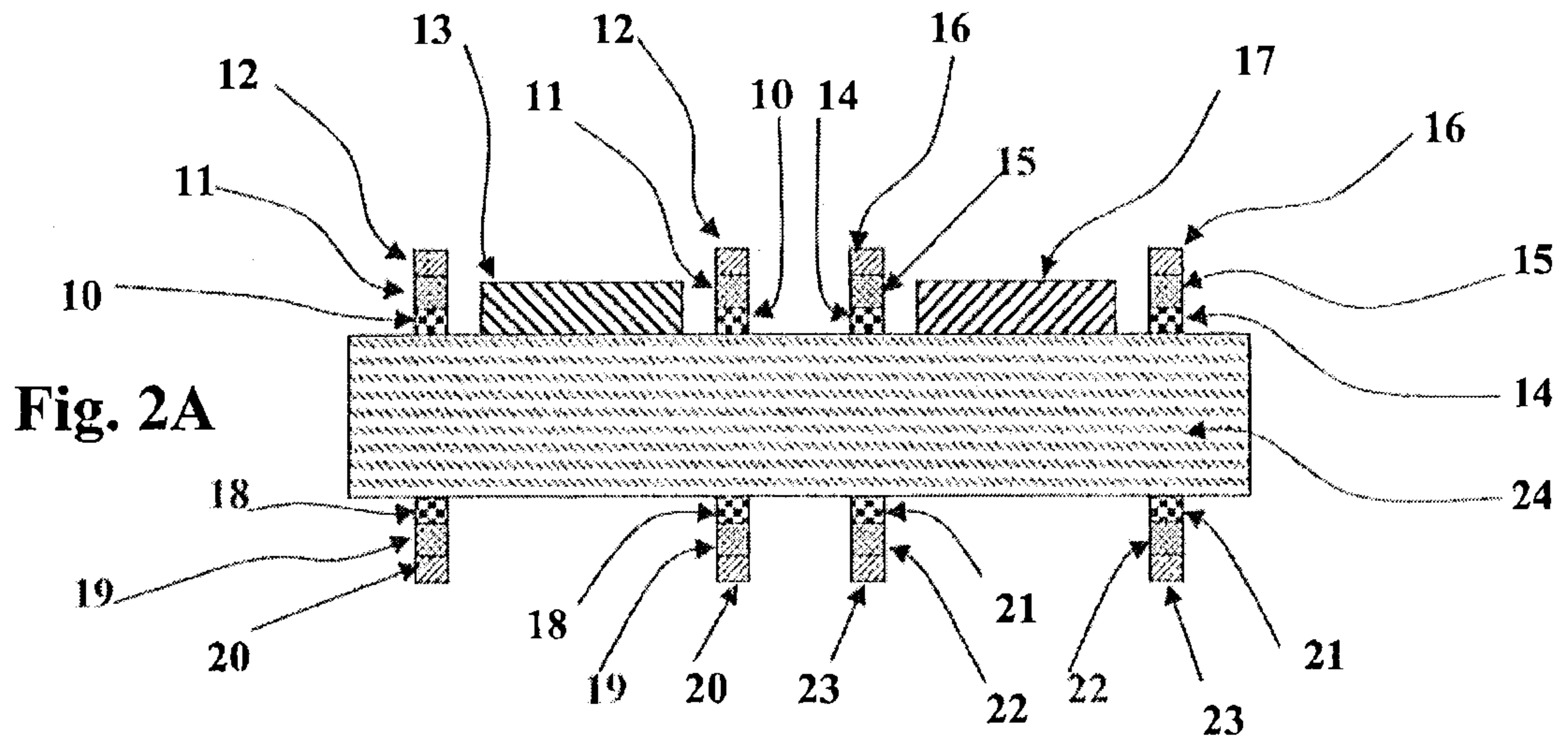
46. The method according to claim 45, wherein applying the bias comprises applying a voltage across the two of the at least two electrodes.

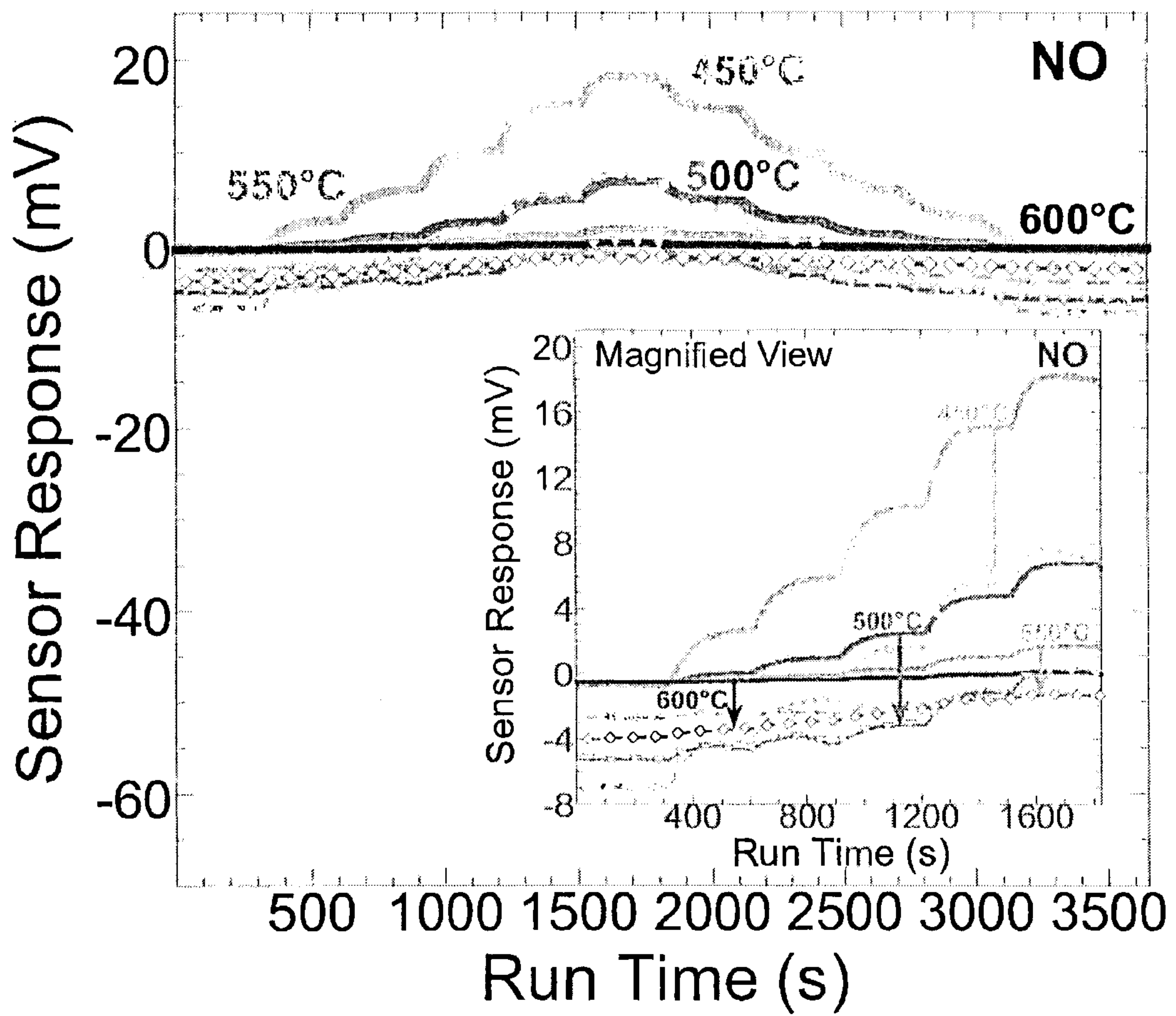
47. The method according to claim 45, wherein applying the bias comprises applying a current across the two of the at least two electrodes.

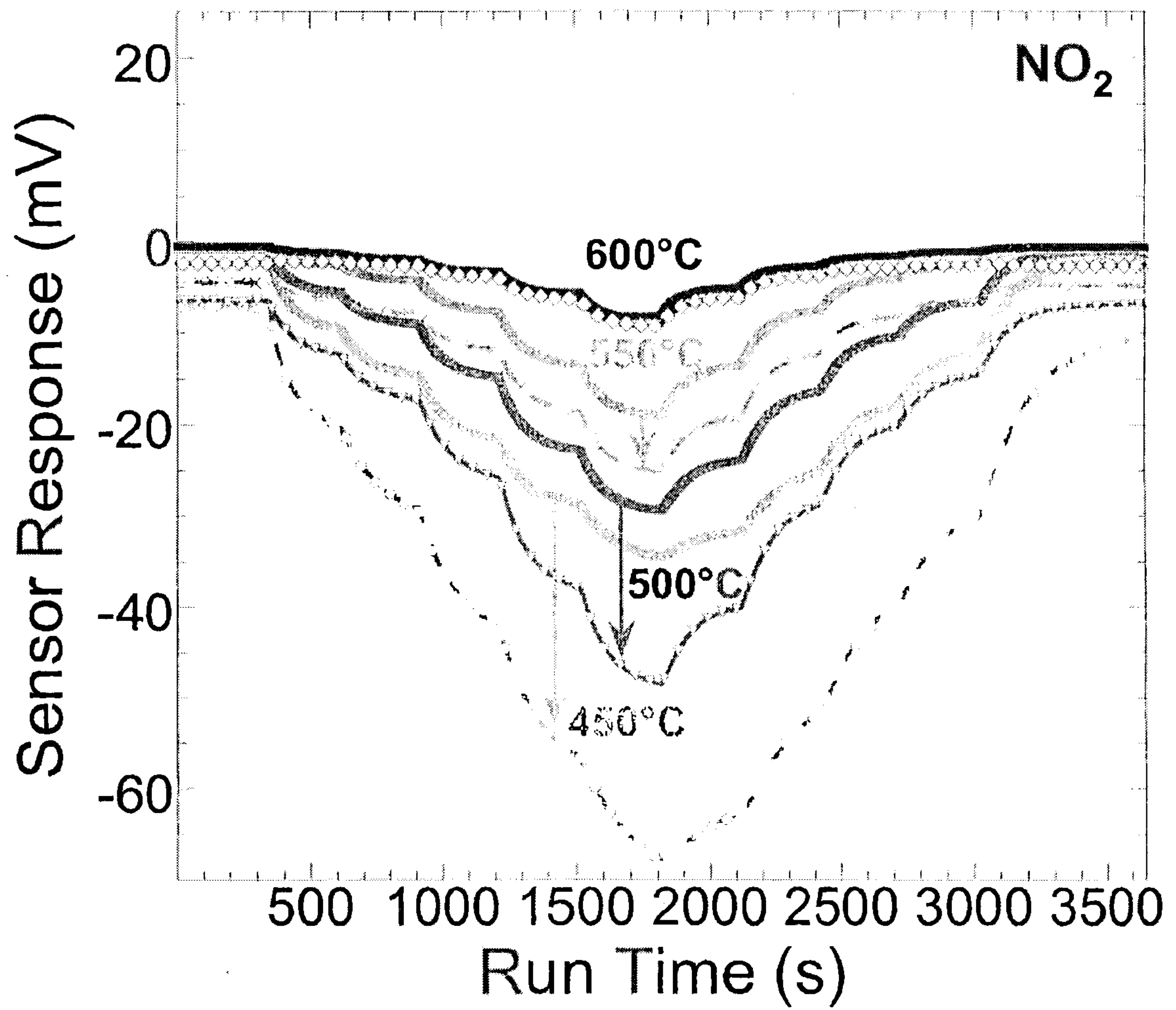
48. The method according to claim 41,
wherein the substrate comprises a porous structure that allows the at least one gas to flow through at least a portion of the porous structure, and
wherein the at least two electrodes comprise a plurality of particles within the porous structure.

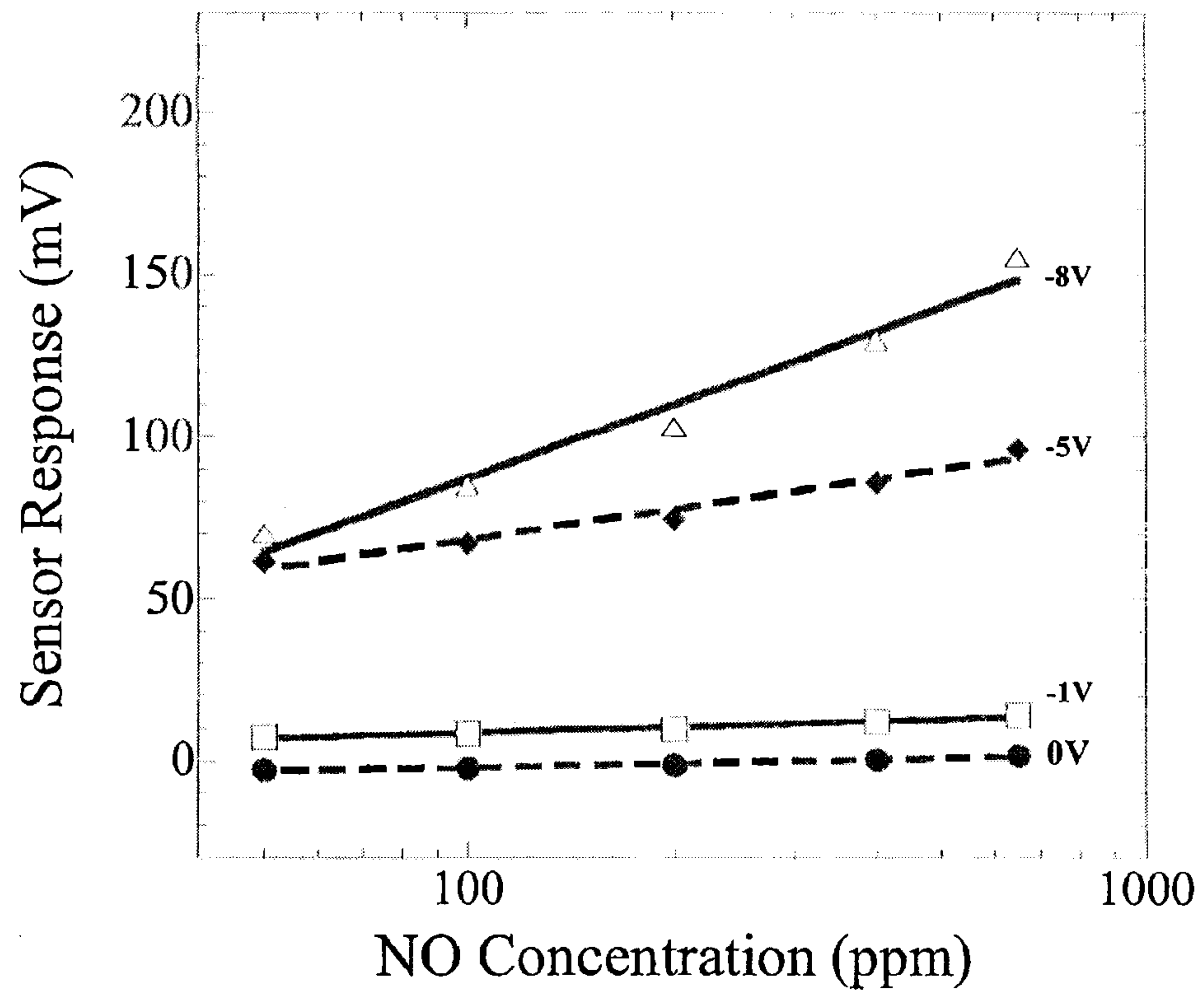
49. A method of modifying a catalysis reaction, comprising:
- providing a substrate, wherein the substrate comprises an electrolyte;
- providing at least two electrodes, wherein the at least two electrodes are in contact with the electrolyte;
- exposing a surface of one or more of the at least two electrodes is exposed to one or more gases, producing an electric field proximate the surface, wherein the electric field modifies a catalysis reaction between the one or more gases and the one or more of the at least two electrodes.
50. The method according to claim 49, wherein the electric field enhances the catalysis reaction between the one or more gases and the one or more of the at least two electrodes.
51. The method according to claim 50, further comprising exposing the electrolyte to the one or more gases, wherein the electric field modifies a catalysis reaction between the one or more gases and the electrolyte.
52. The method according to claim 49, further comprising exposing the electrolyte to the one or more gases, wherein the electric field modifies a catalysis reaction between the one or more gases and the electrolyte.
53. The method according to claim 50, further comprising: applying a bias across two of the at least two electrodes.
54. The method according to claim 53, wherein applying the bias comprises applying a voltage across the two of the at least two electrodes.





**Fig. 3A**

**Fig. 3B**

**Fig. 3C**

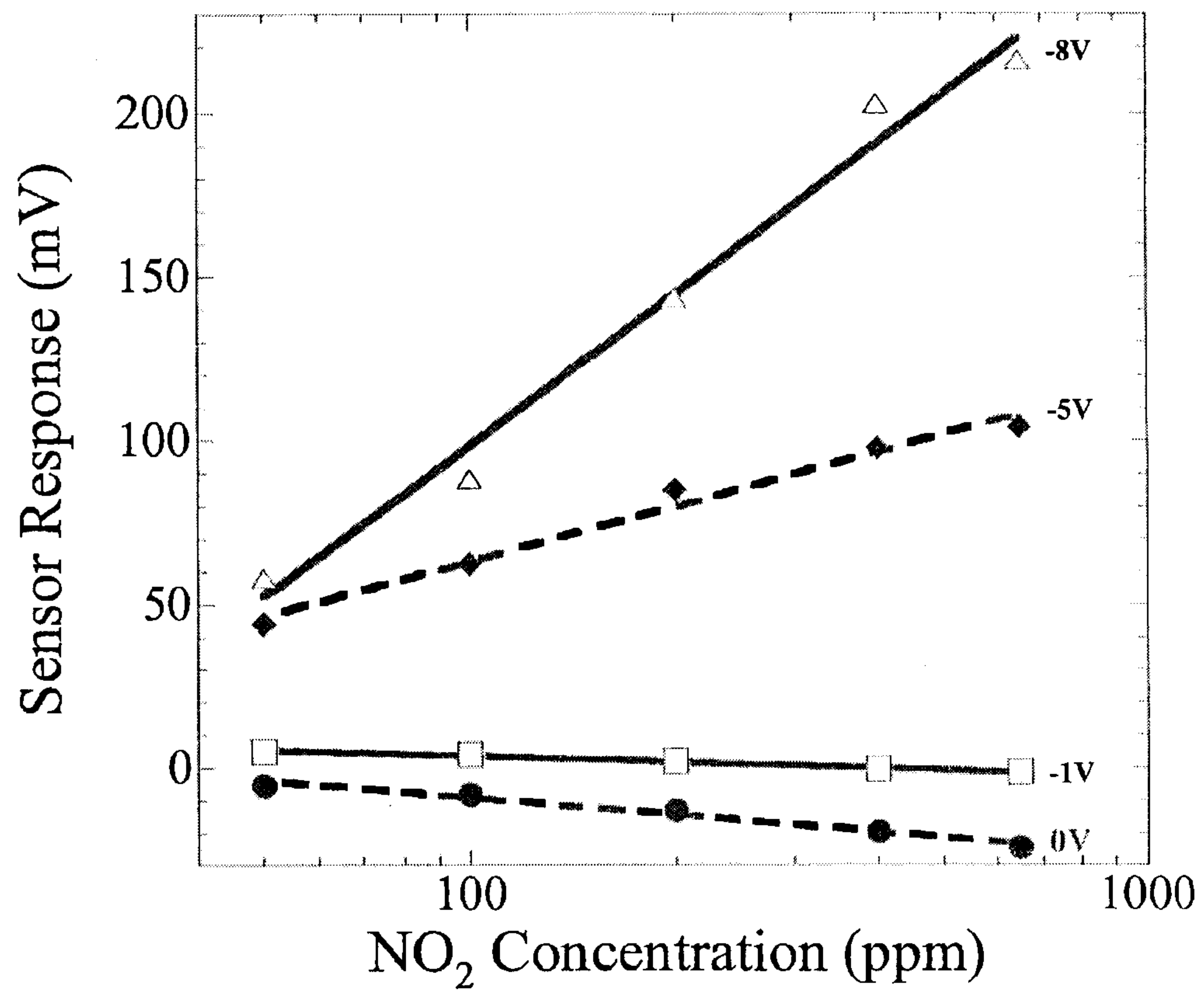


Fig. 3D

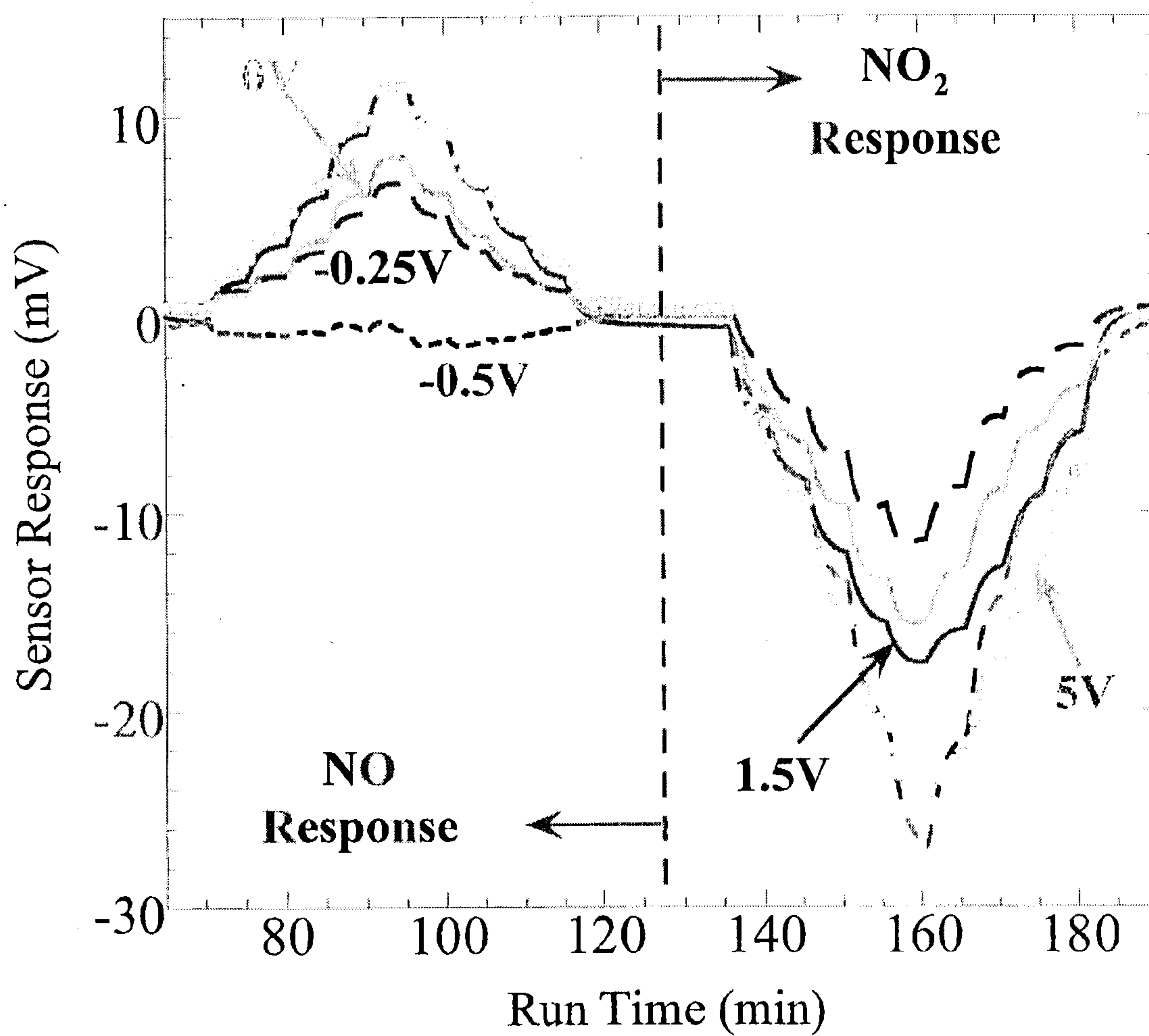
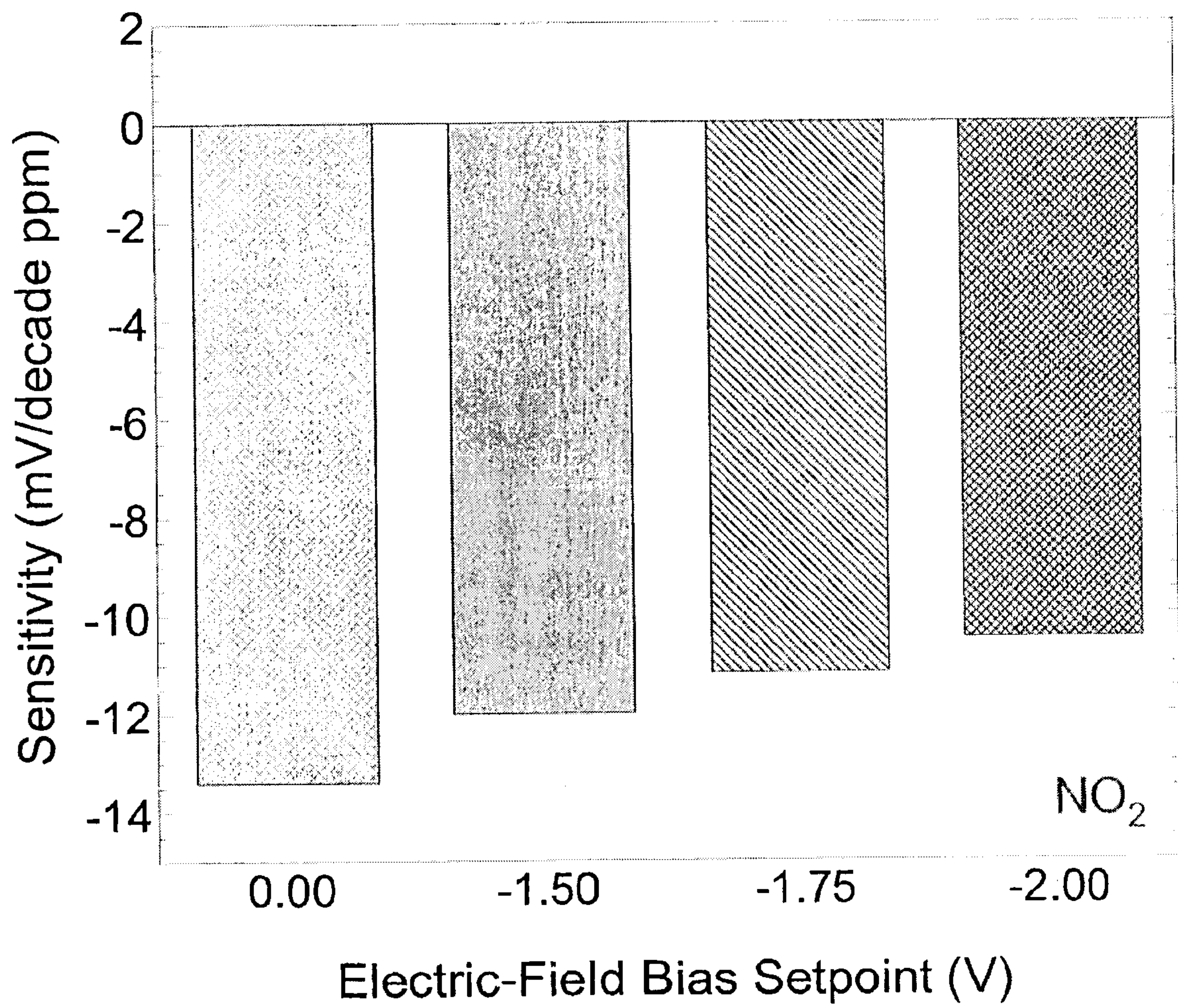
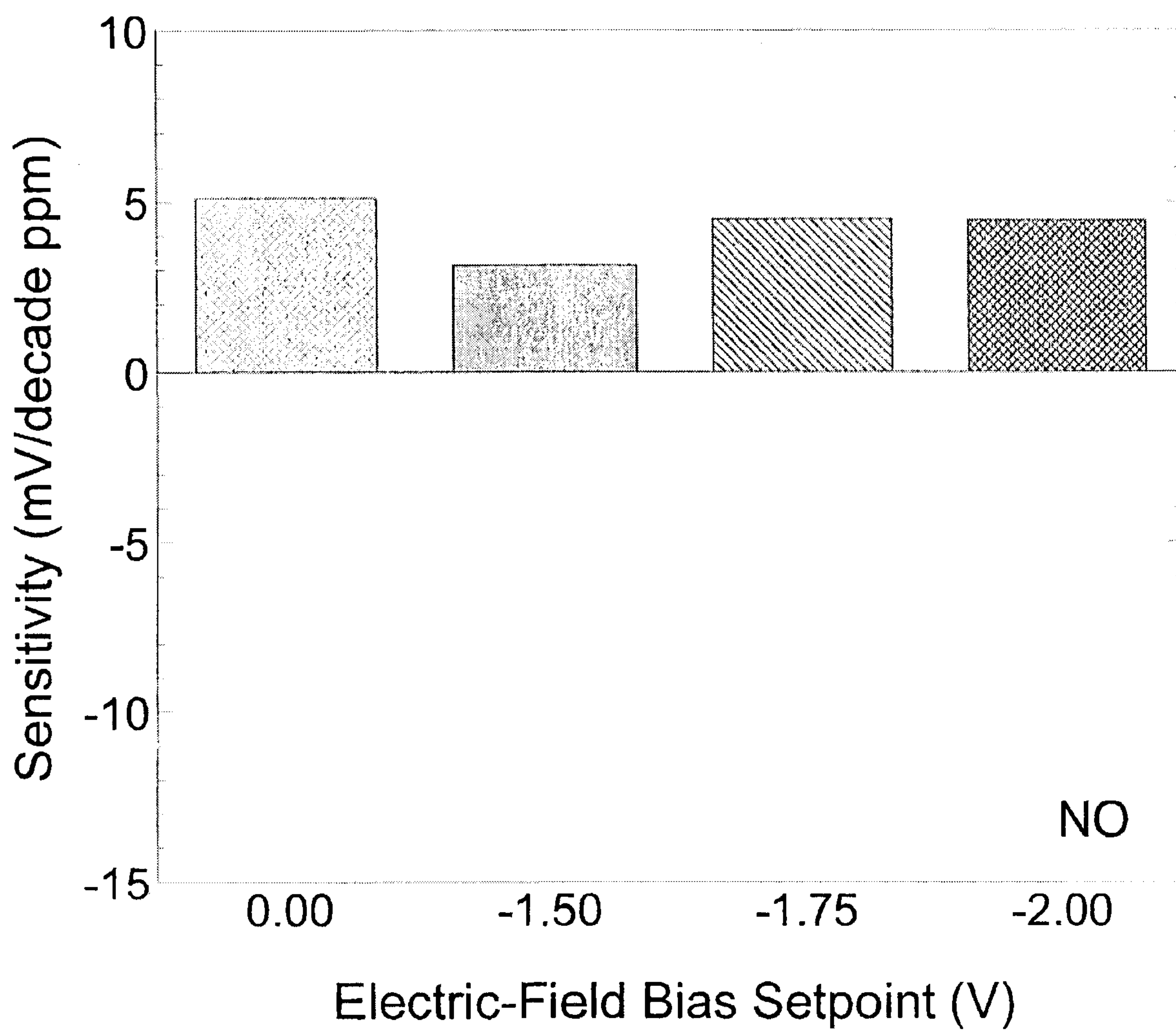
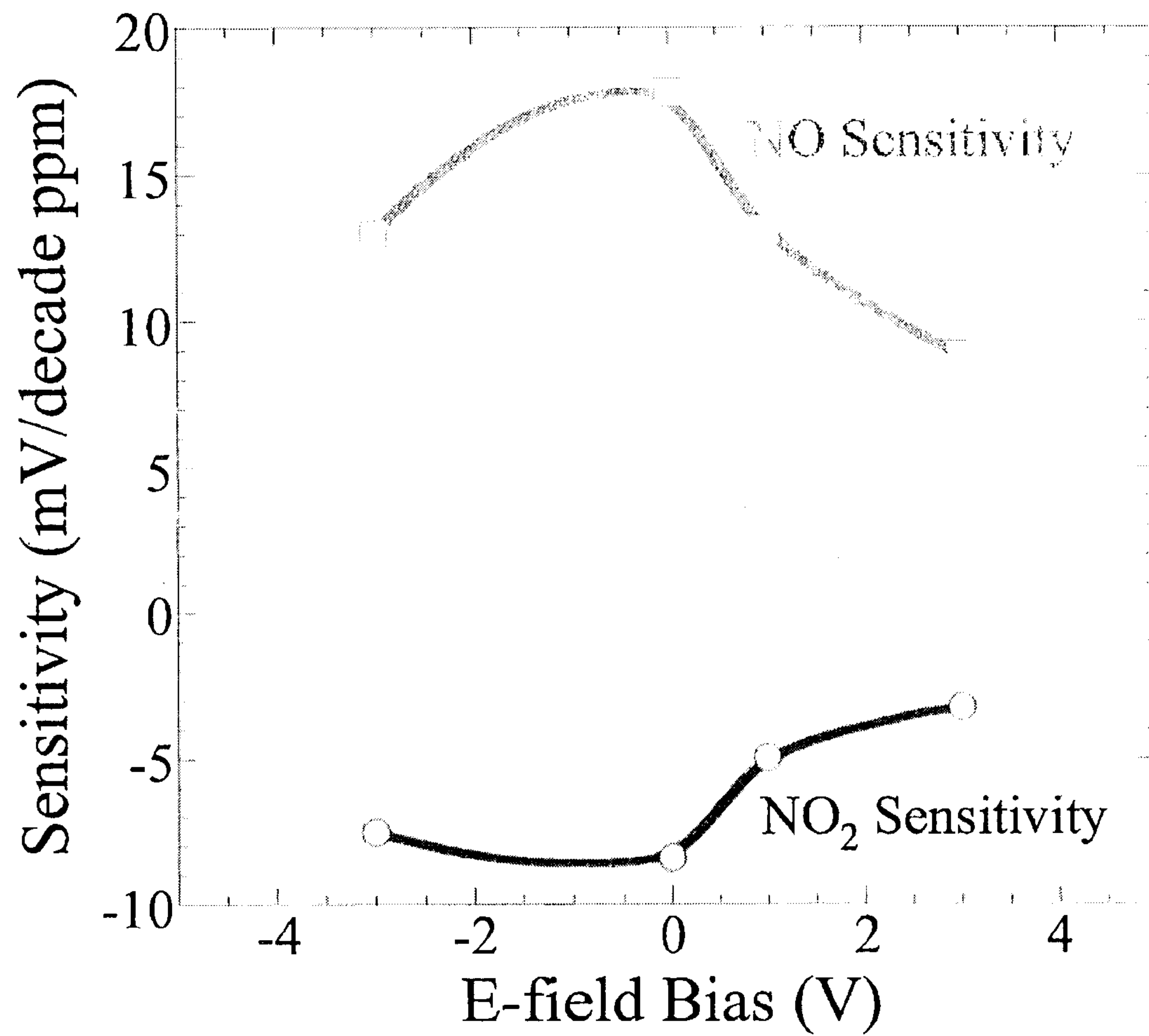


Fig. 3E

**Fig. 3F**

**Fig. 3G**

**Fig. 3H**

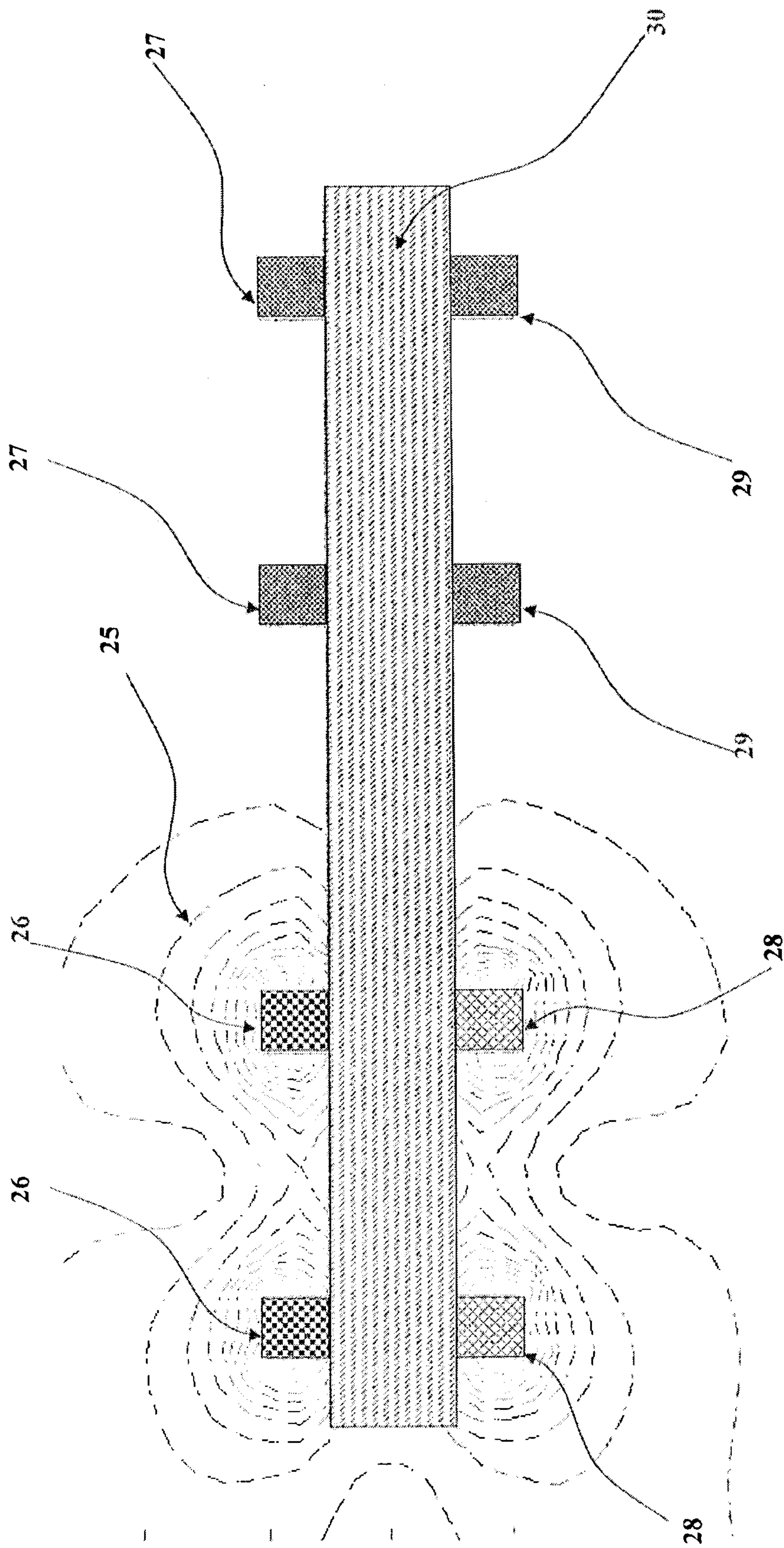


Fig. 4A

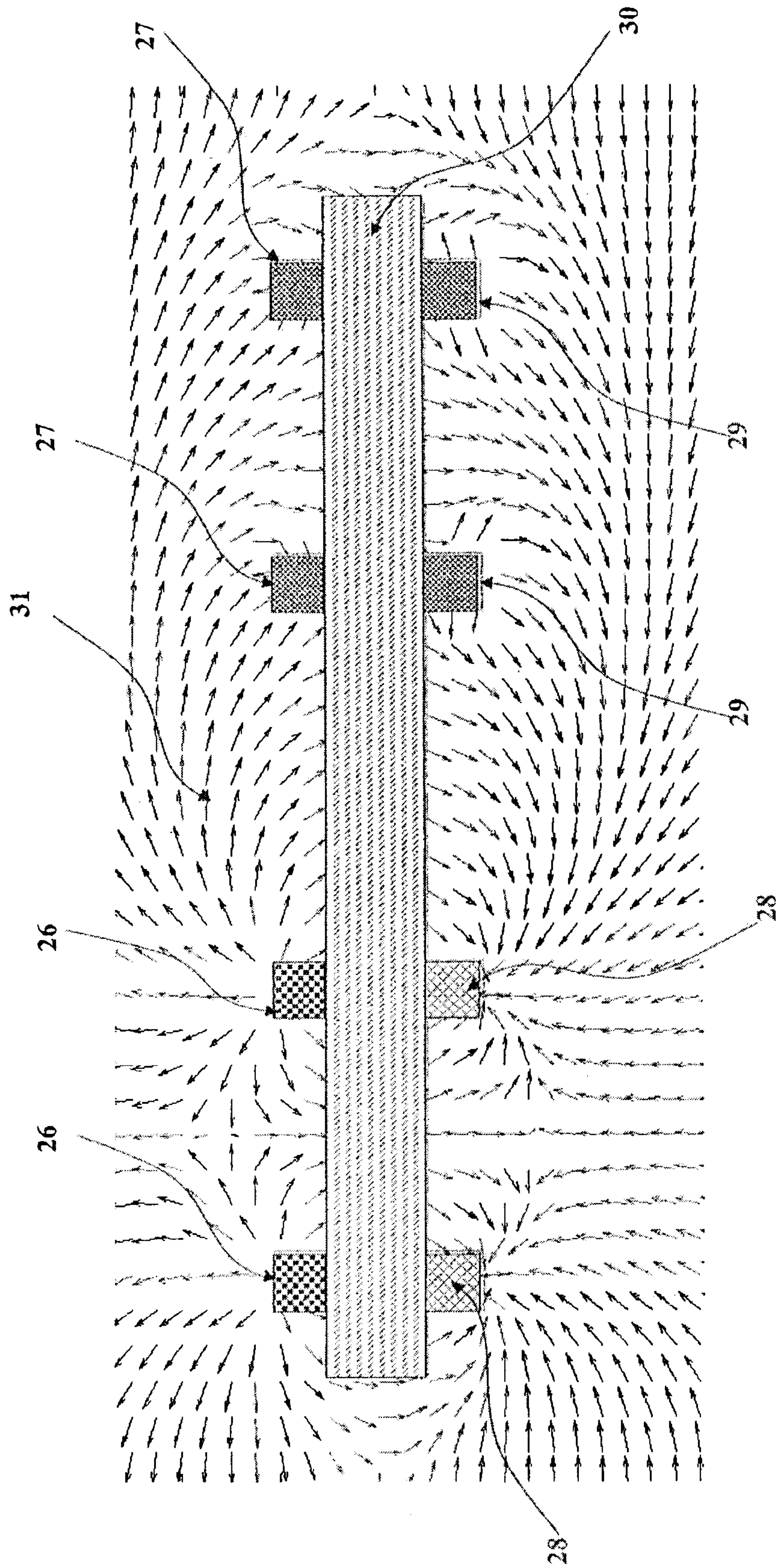


Fig. 4B

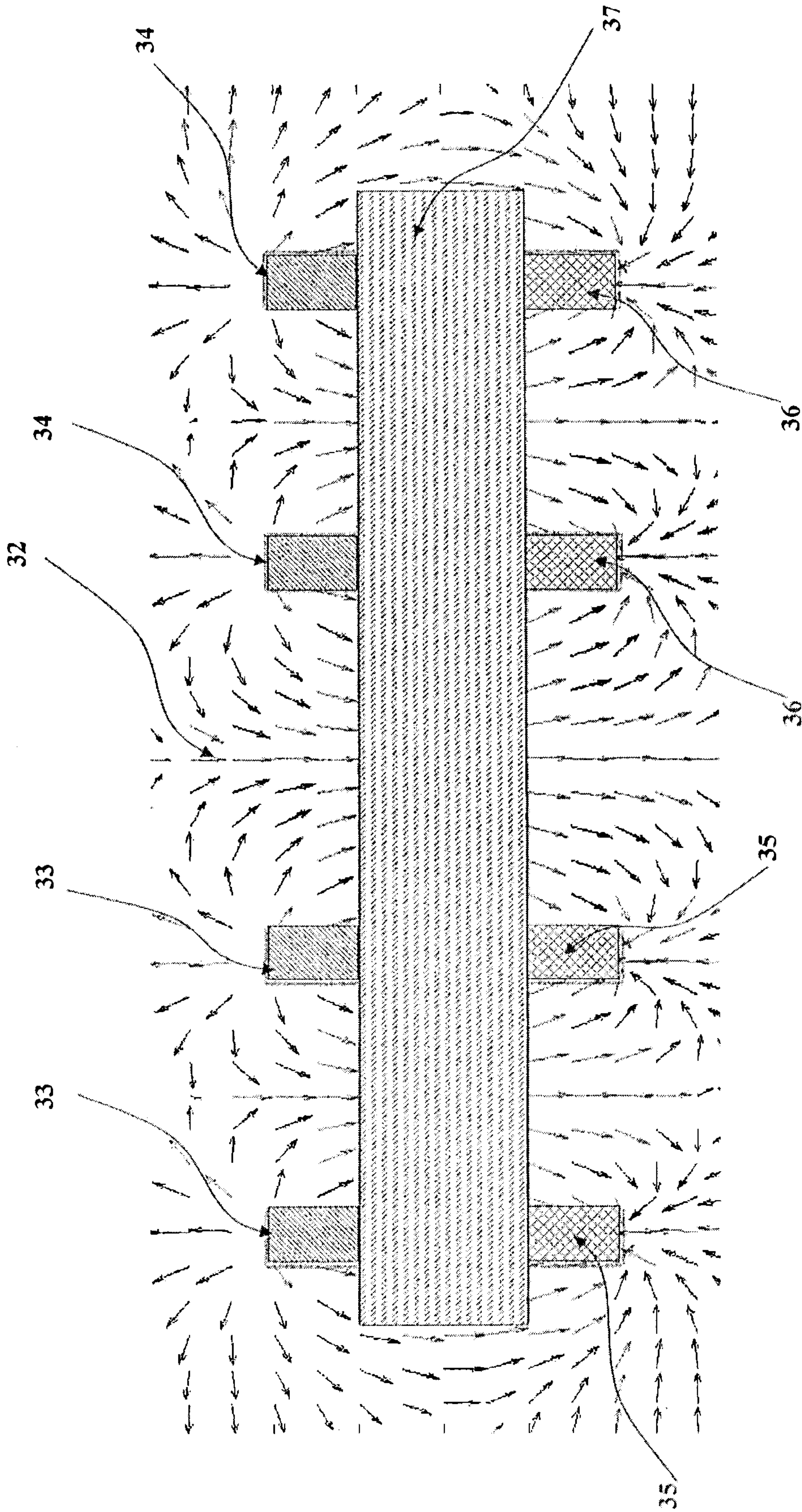


Fig. 4C

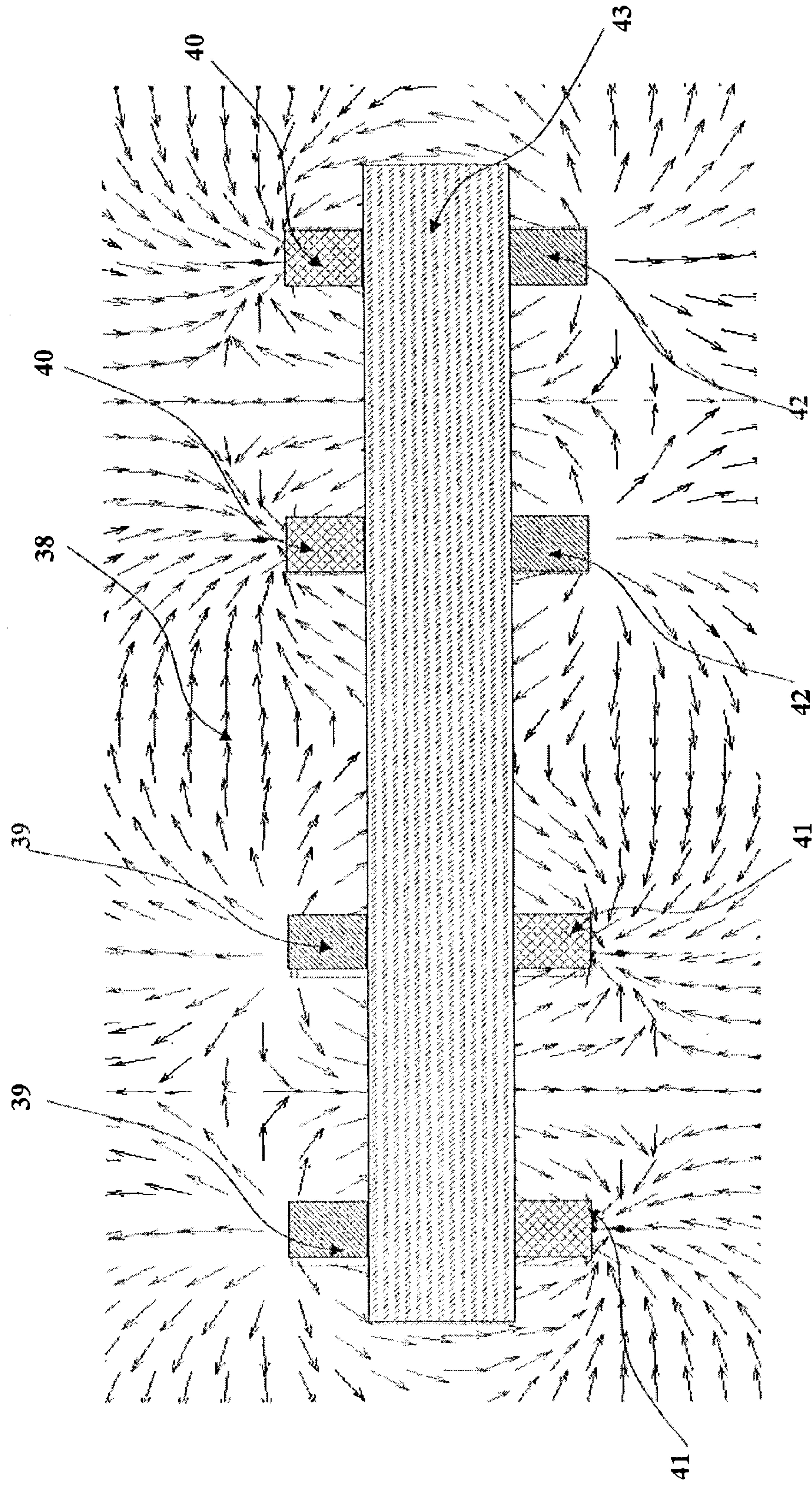
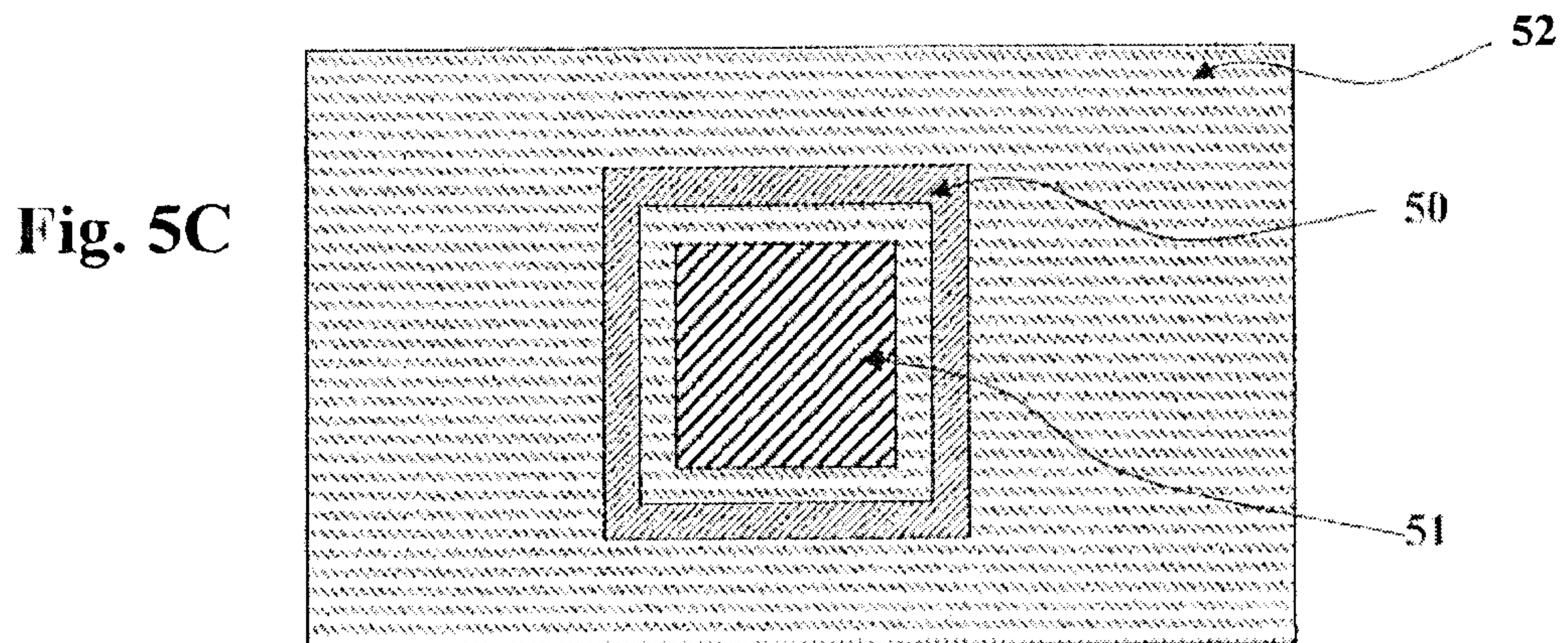
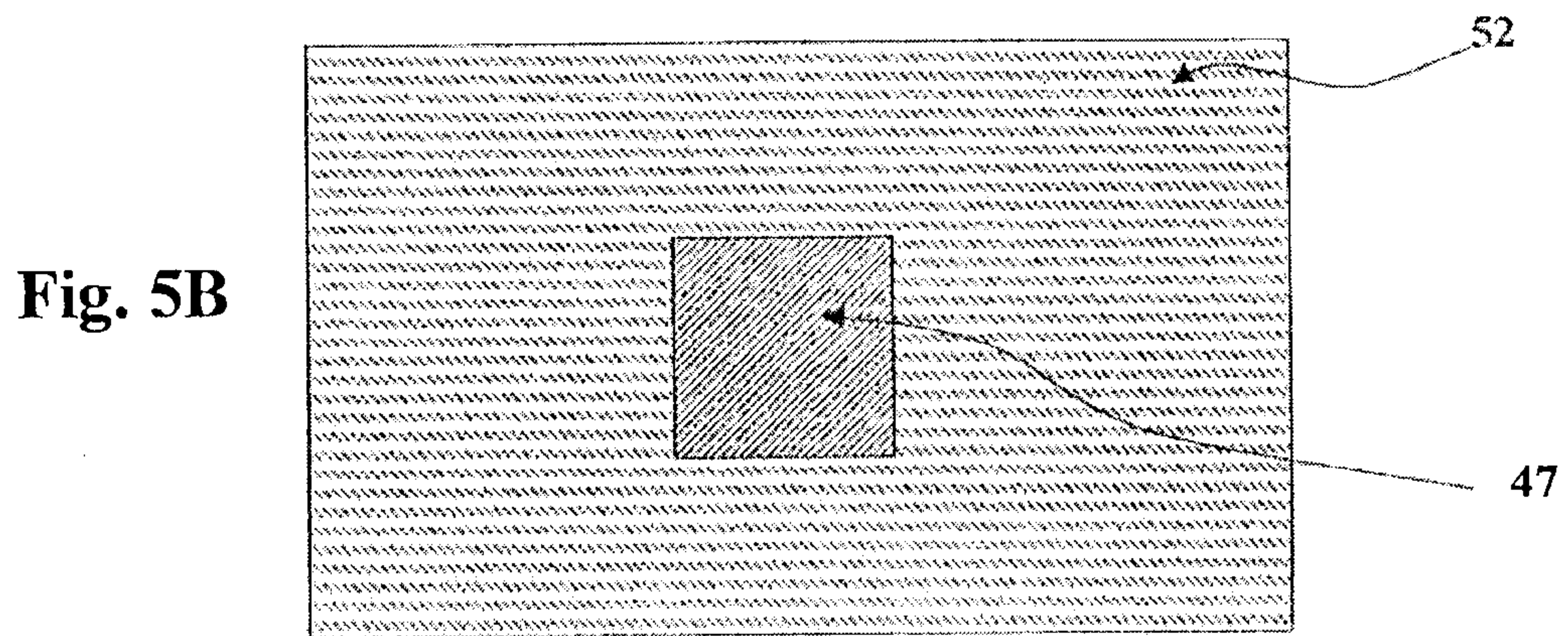
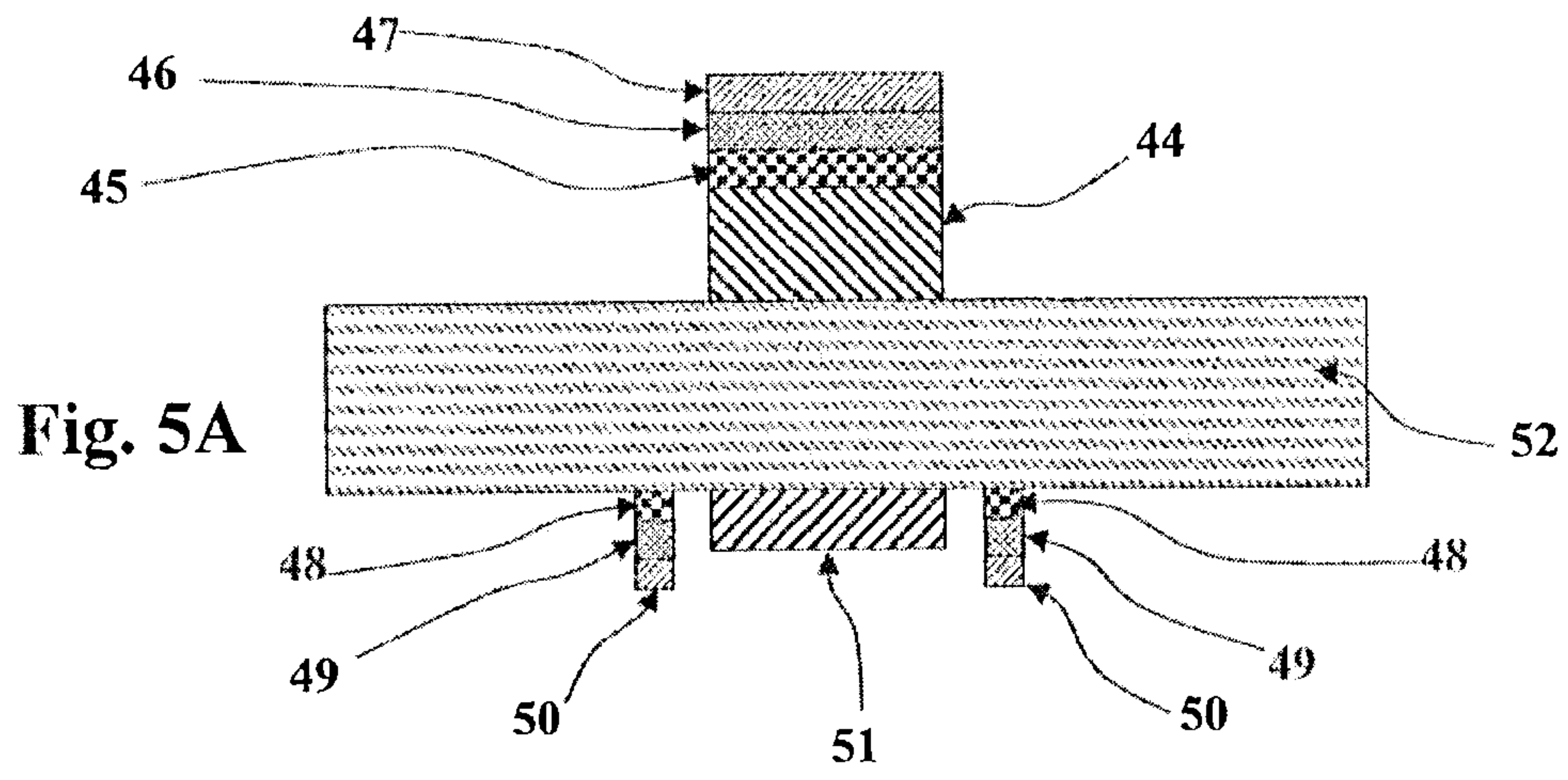


Fig. 4D



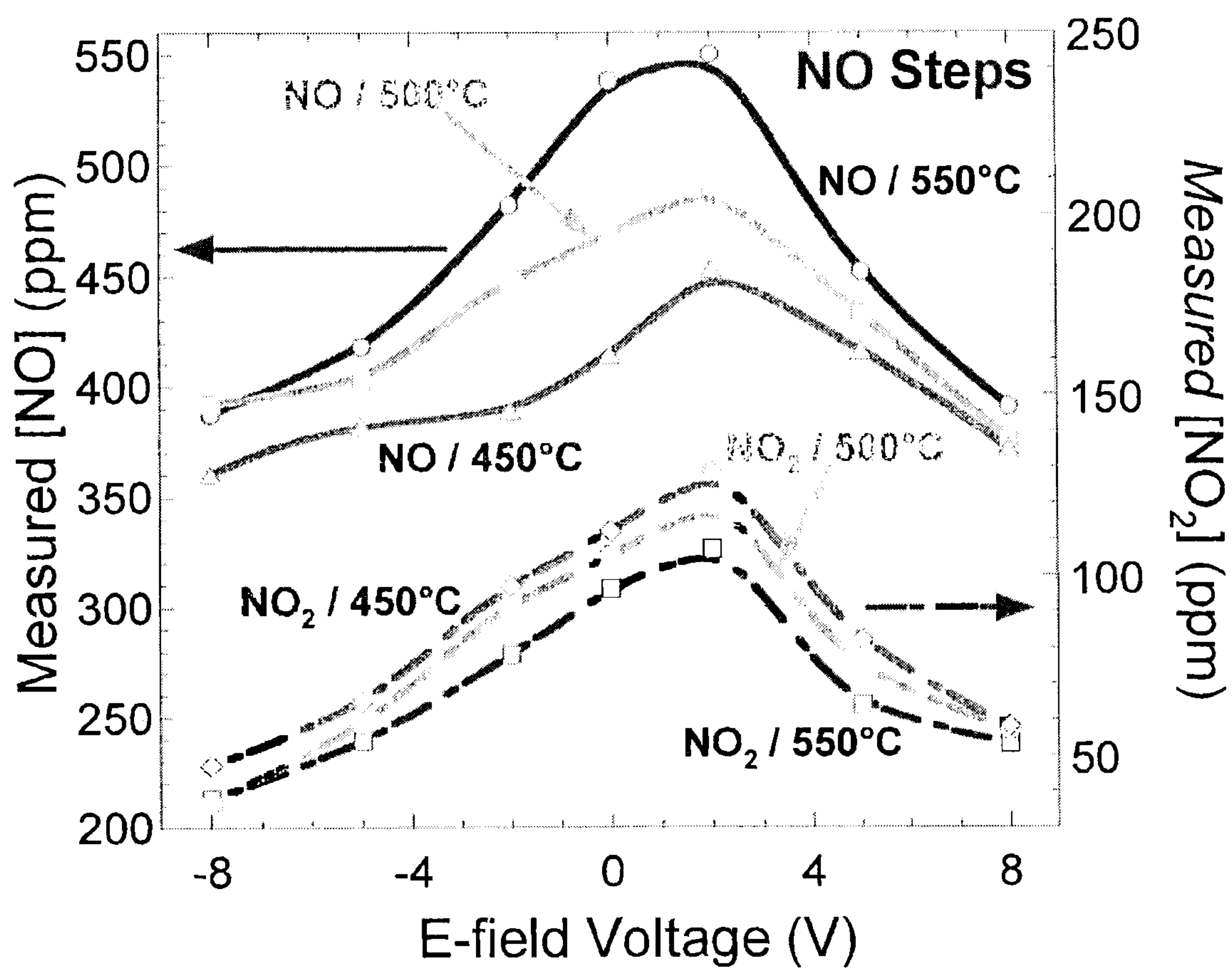
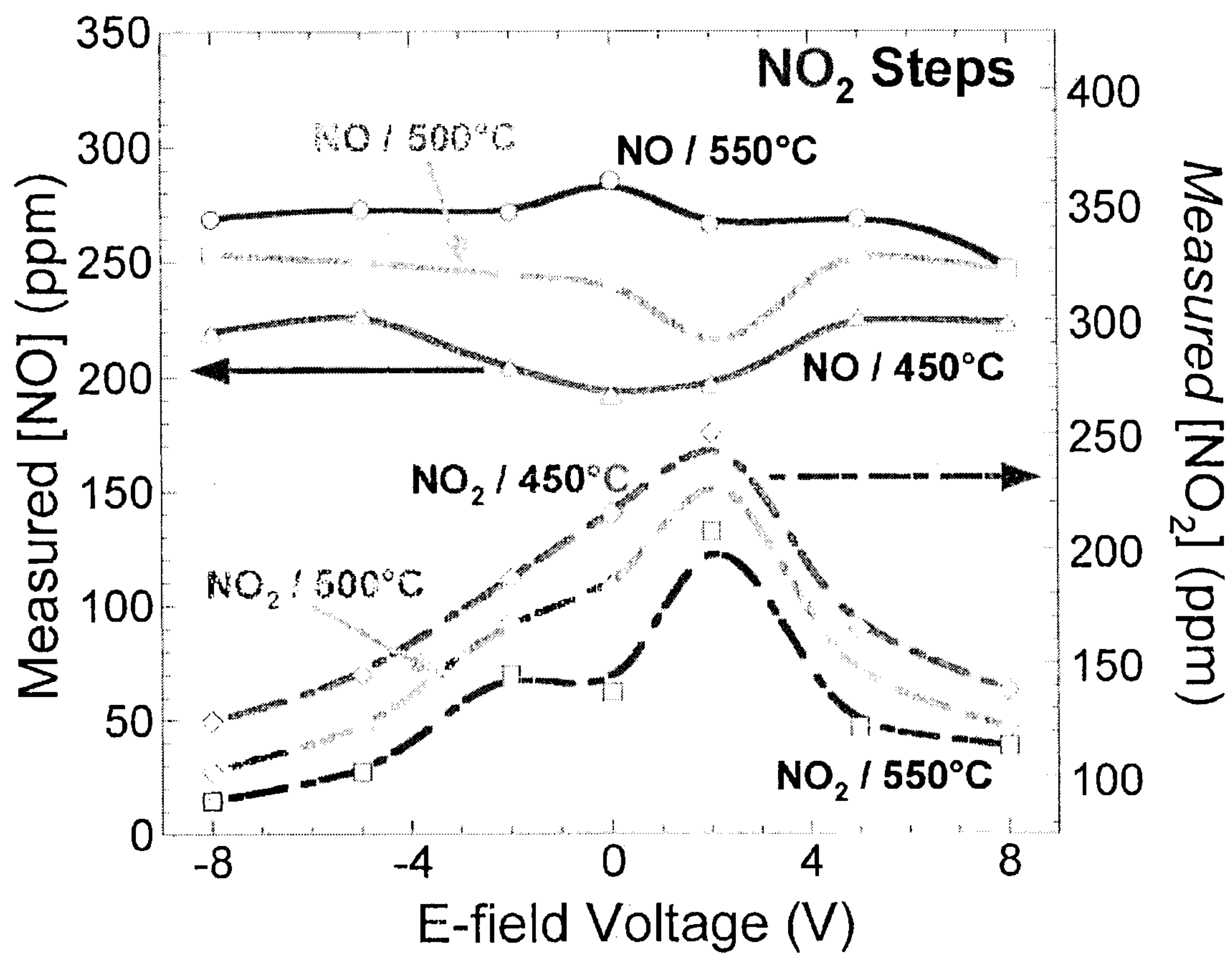


Fig. 6A

**Fig. 6B**

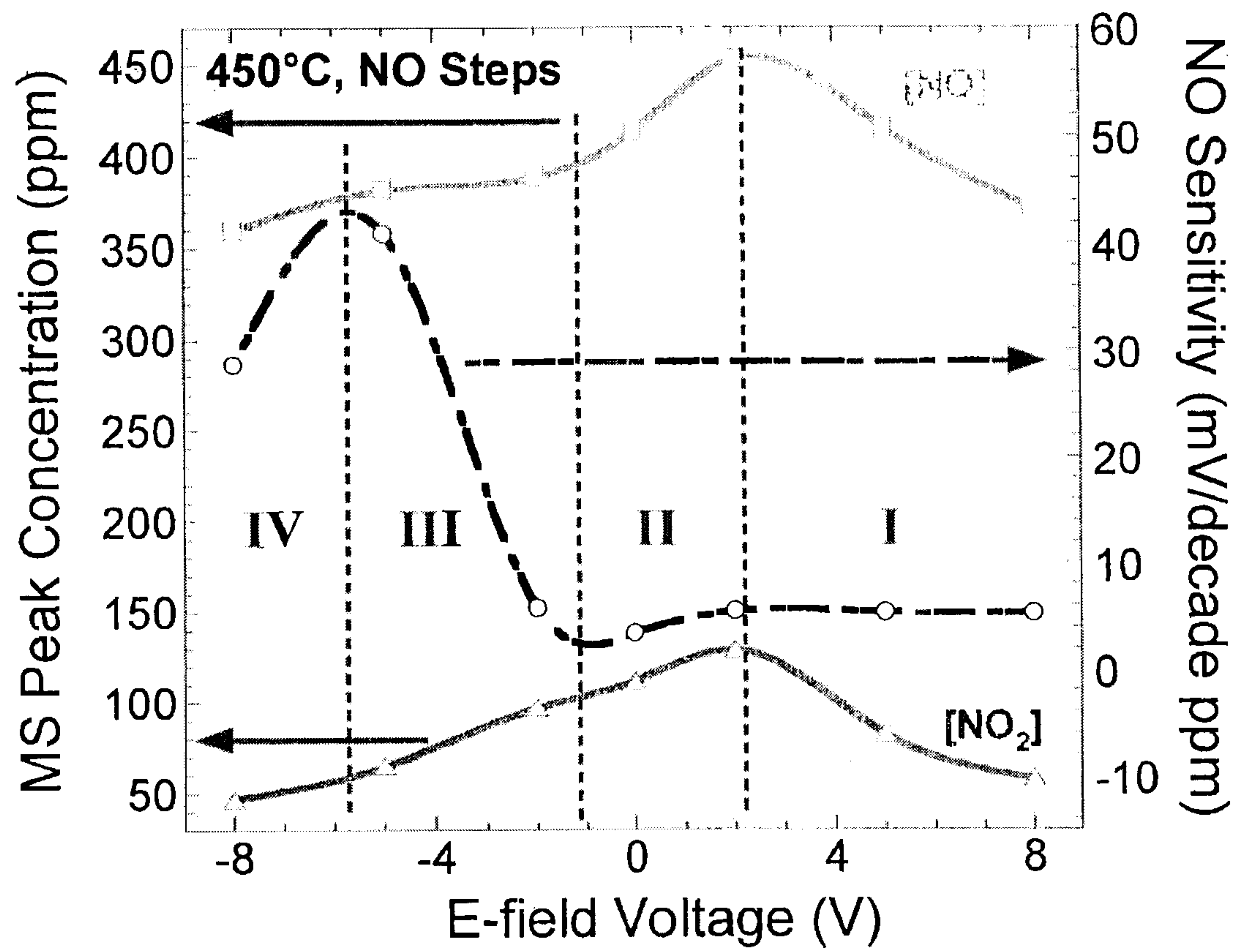


Fig. 6C

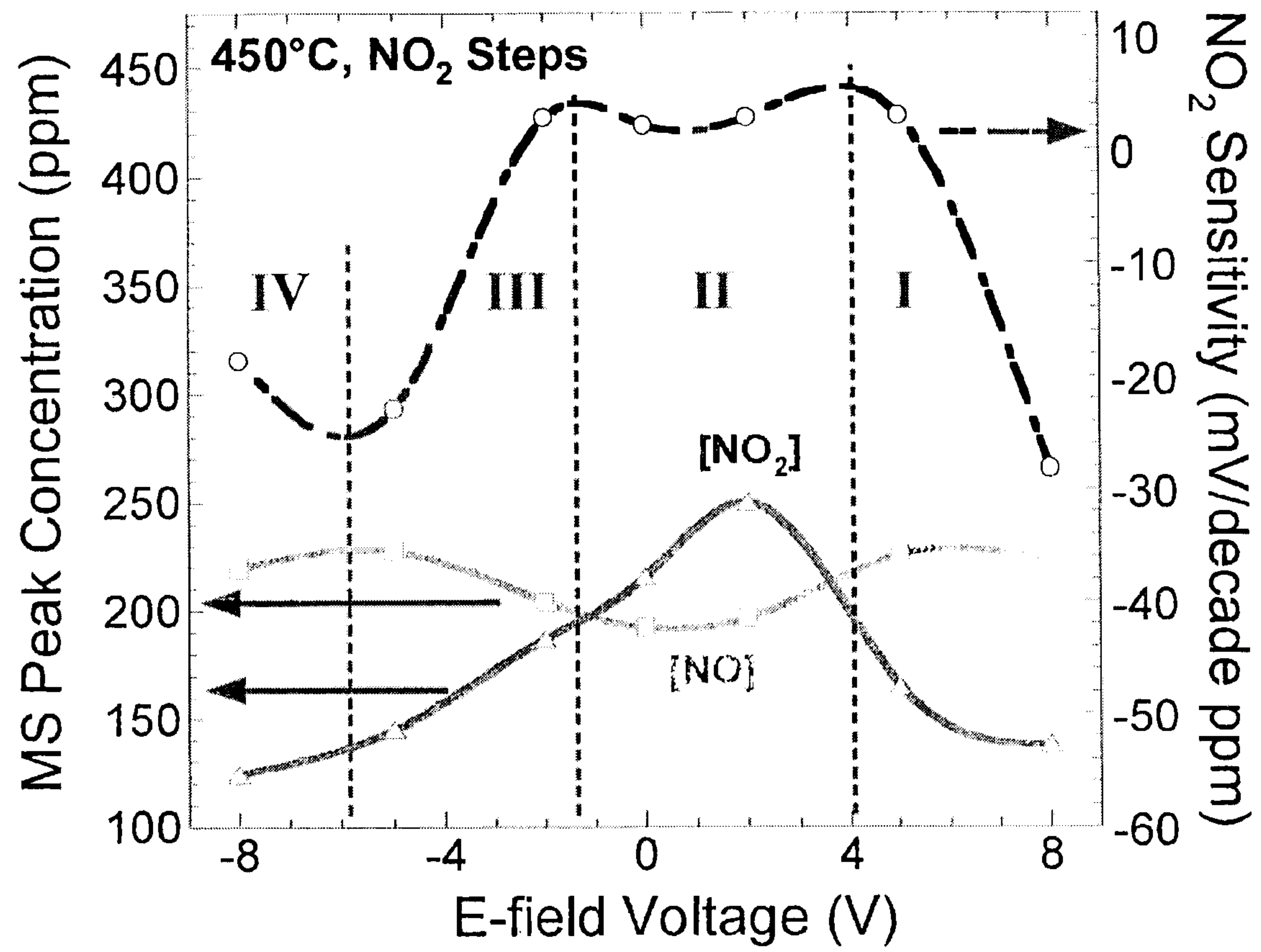
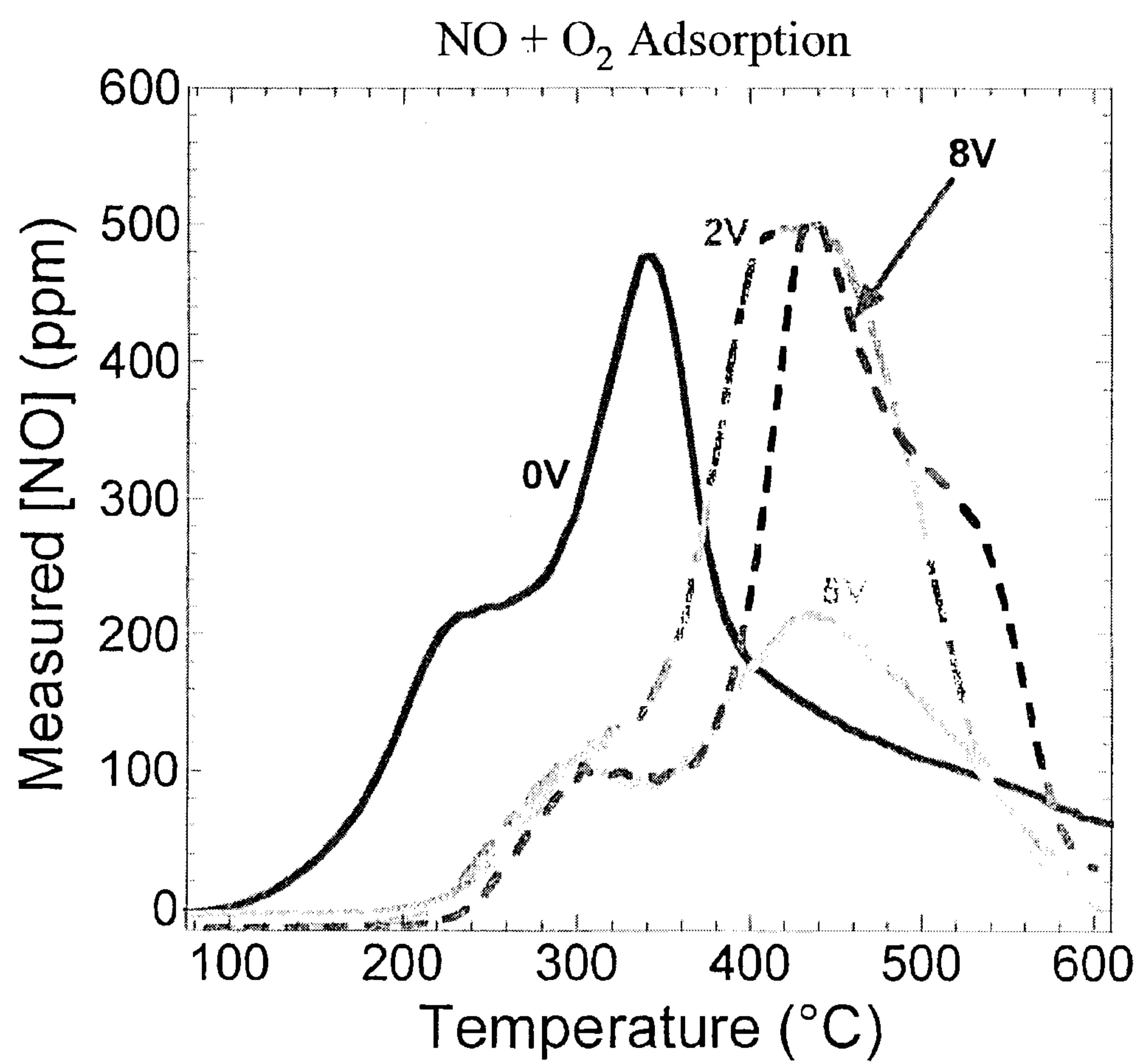
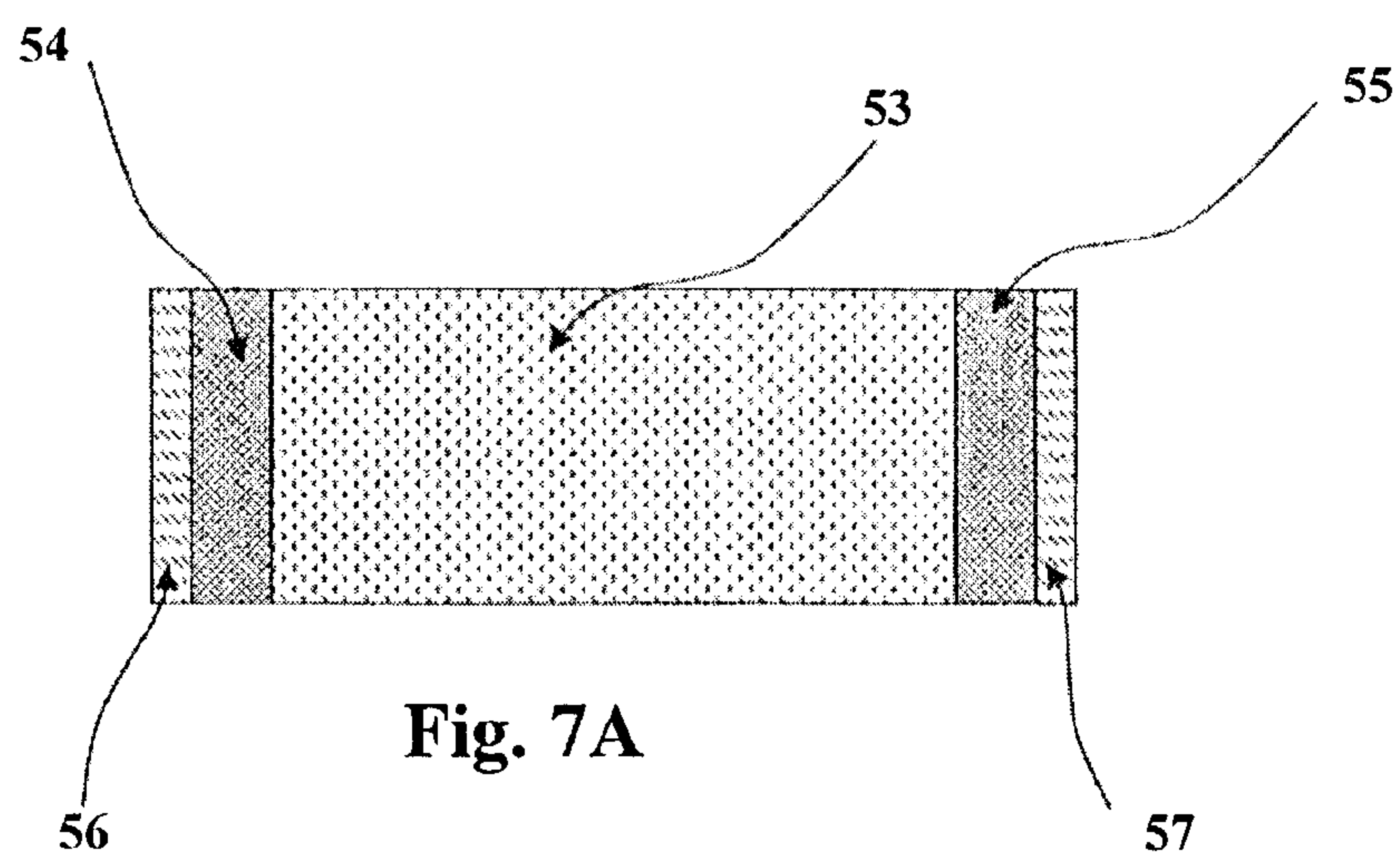


Fig. 6D



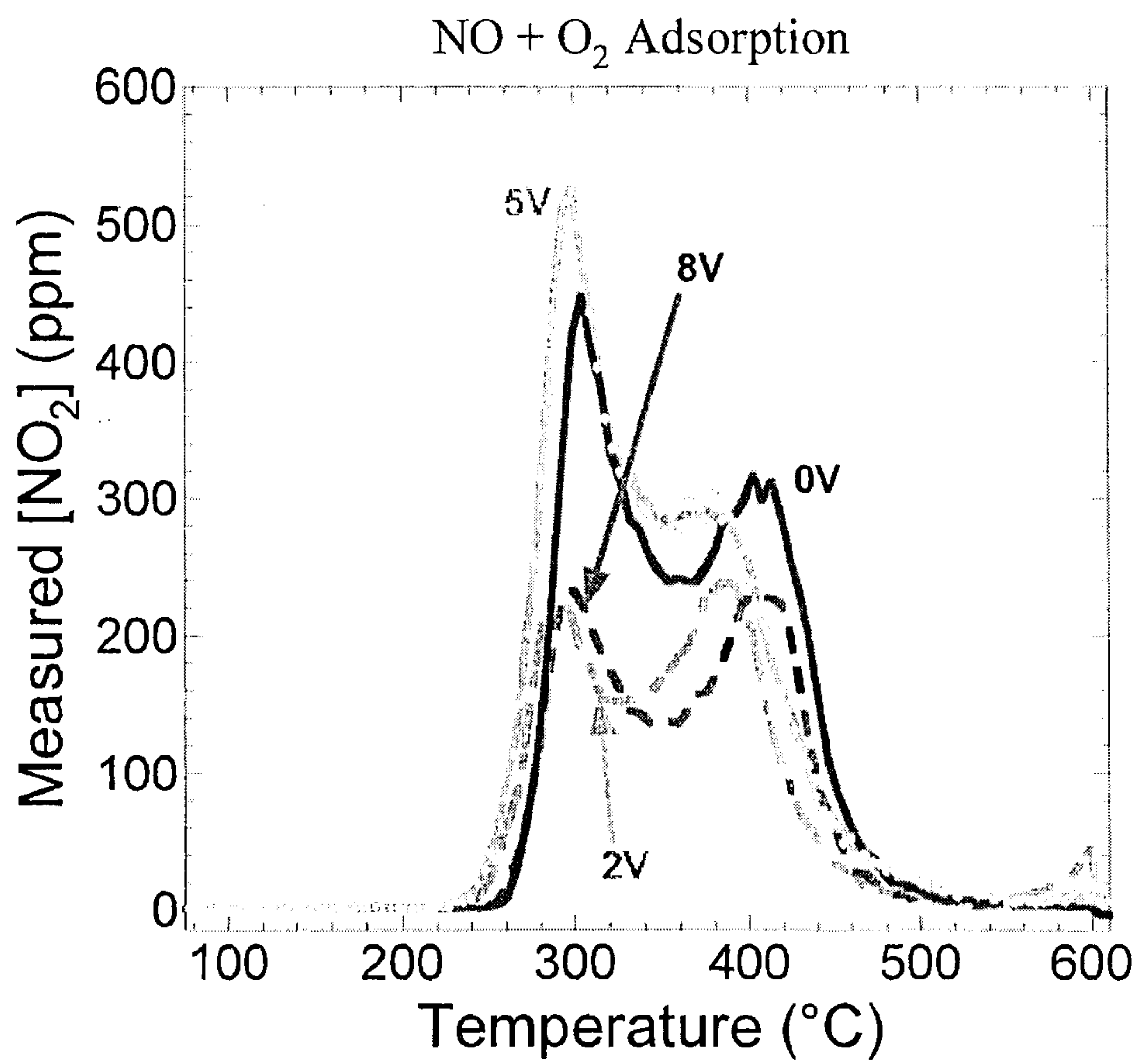
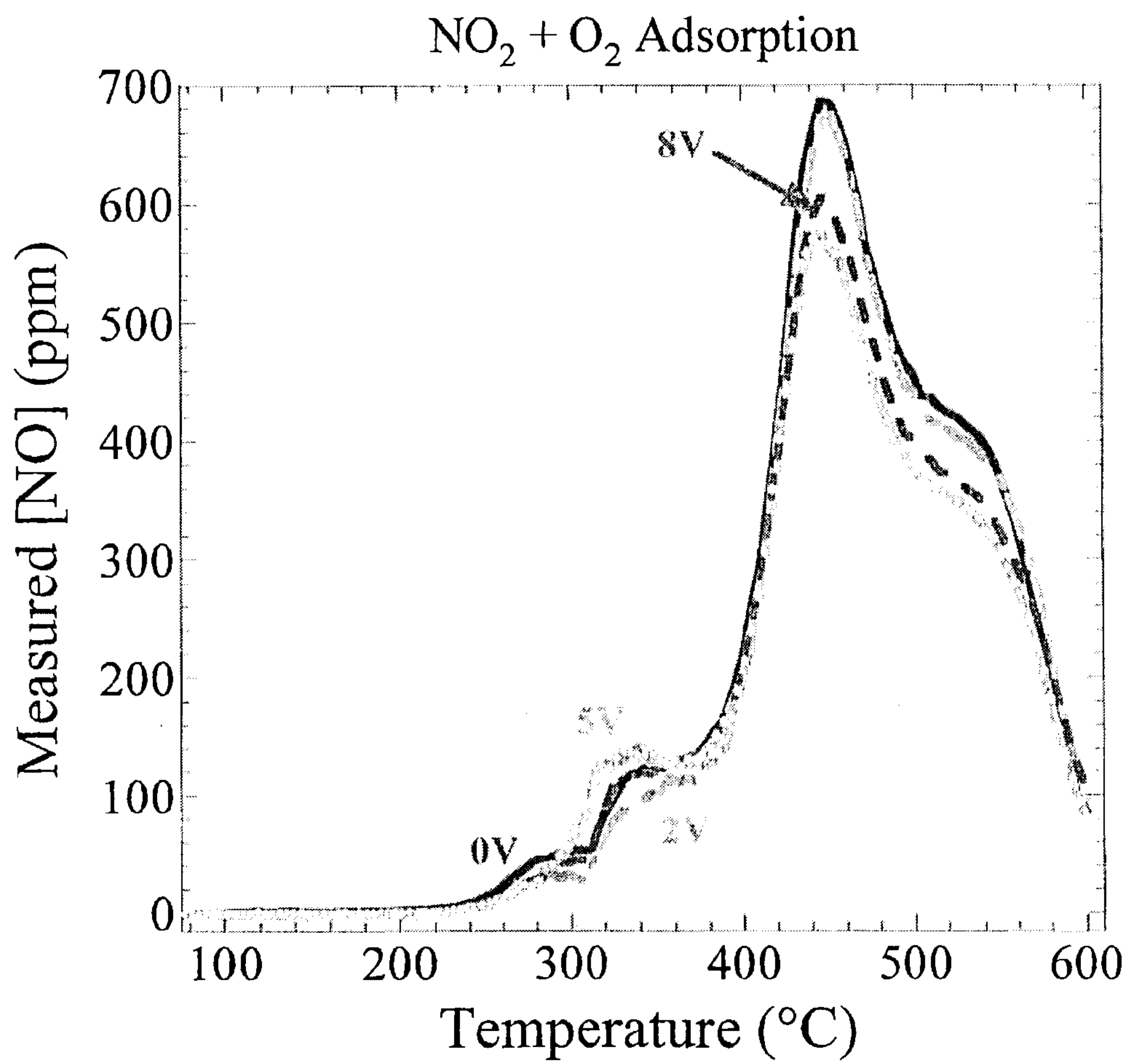


Fig. 7C

**Fig. 7D**

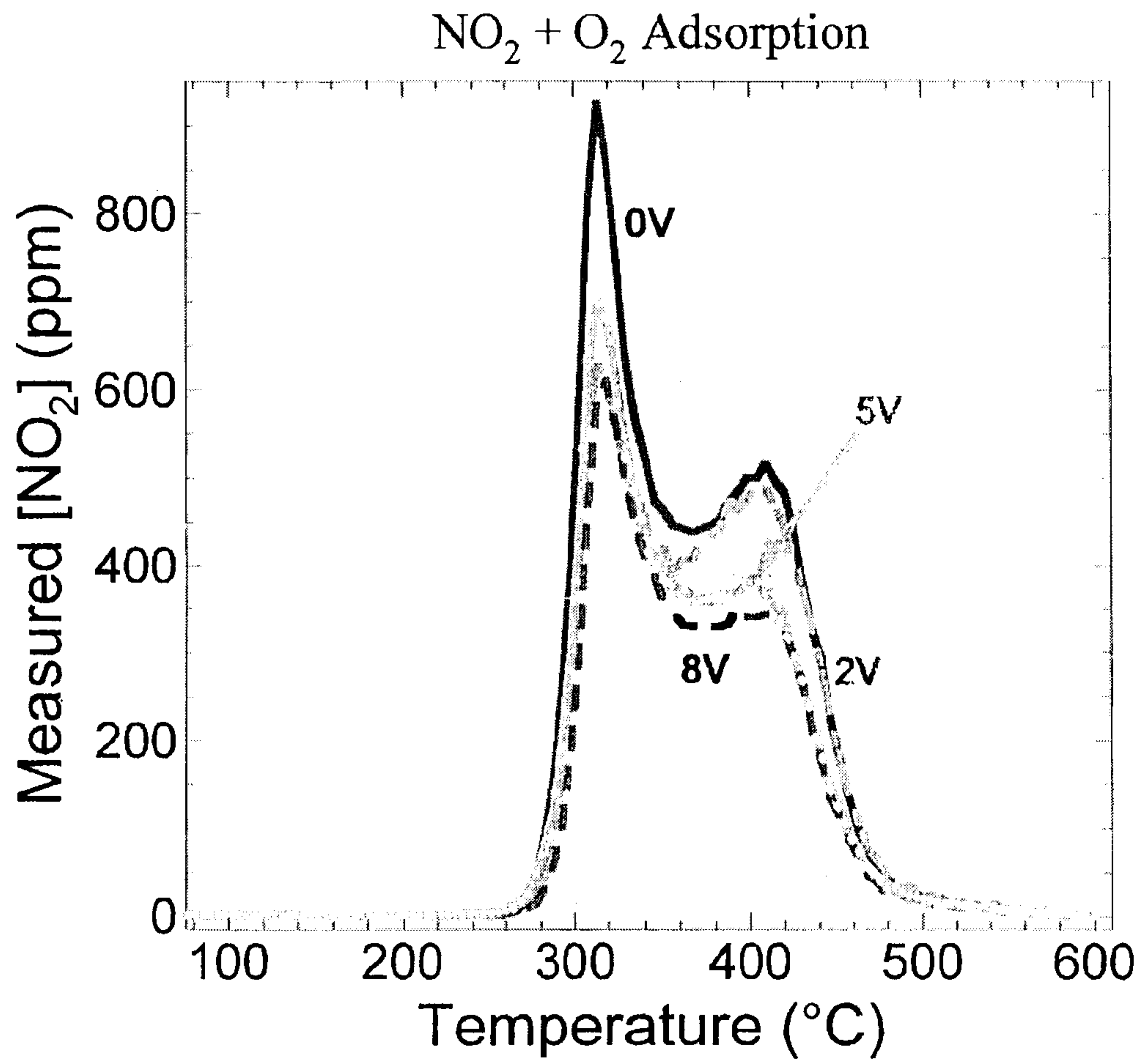


Fig. 7E

