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(54) **POROUS MATERIALS**

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(57) **ABSTRACT**

A porous membrane material comprising a porous mem-
brane substrate coated with a thin, uniform coating of a
metal or metal alloy. The membrane material can have high
electrical conductivity. The membrane material can exhibit
a very high ratio of electrical conductivity to thermal con-
ductivity. The porous membrane substrate may be removed
to form the membrane.

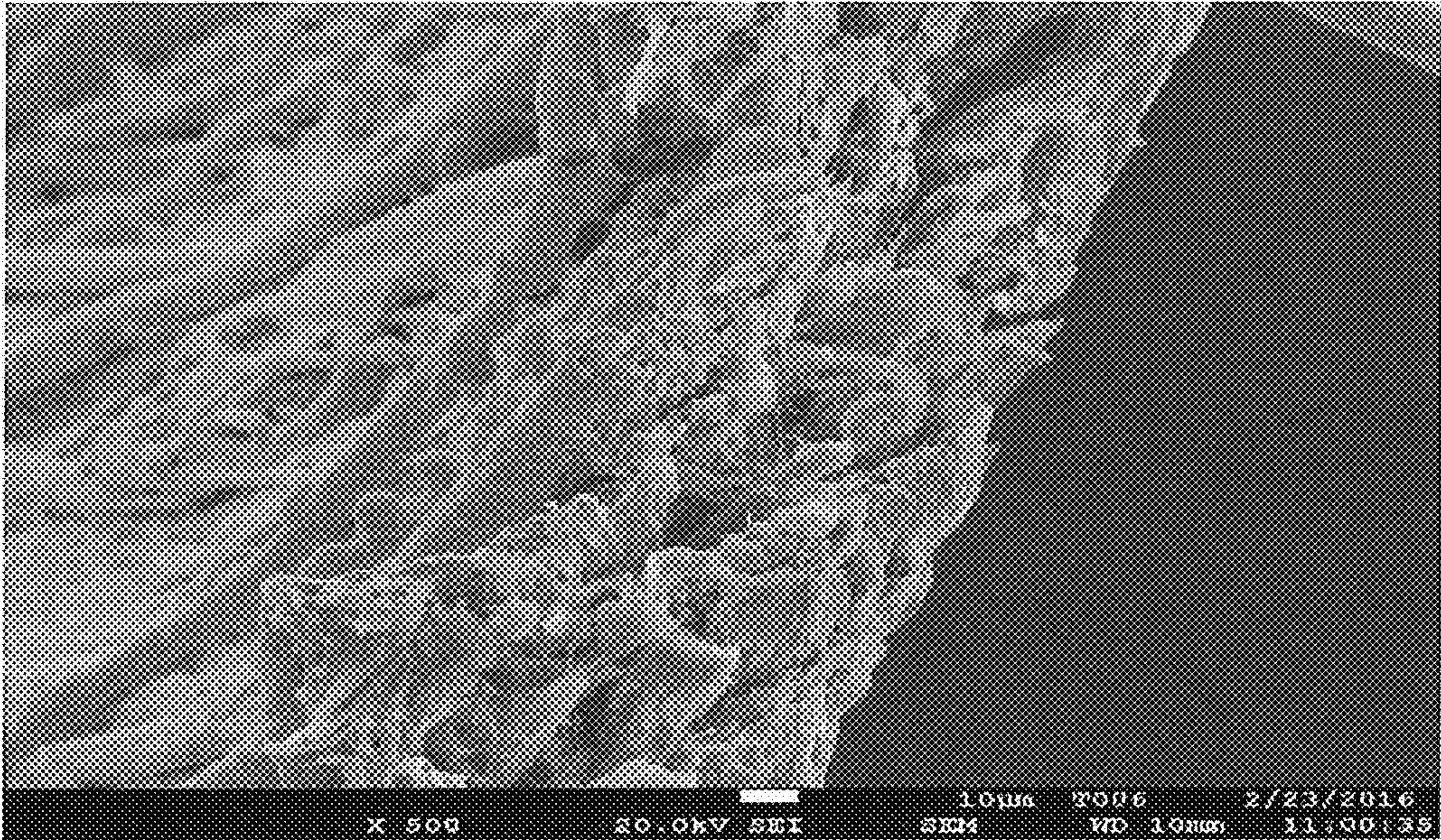


FIGURE 1

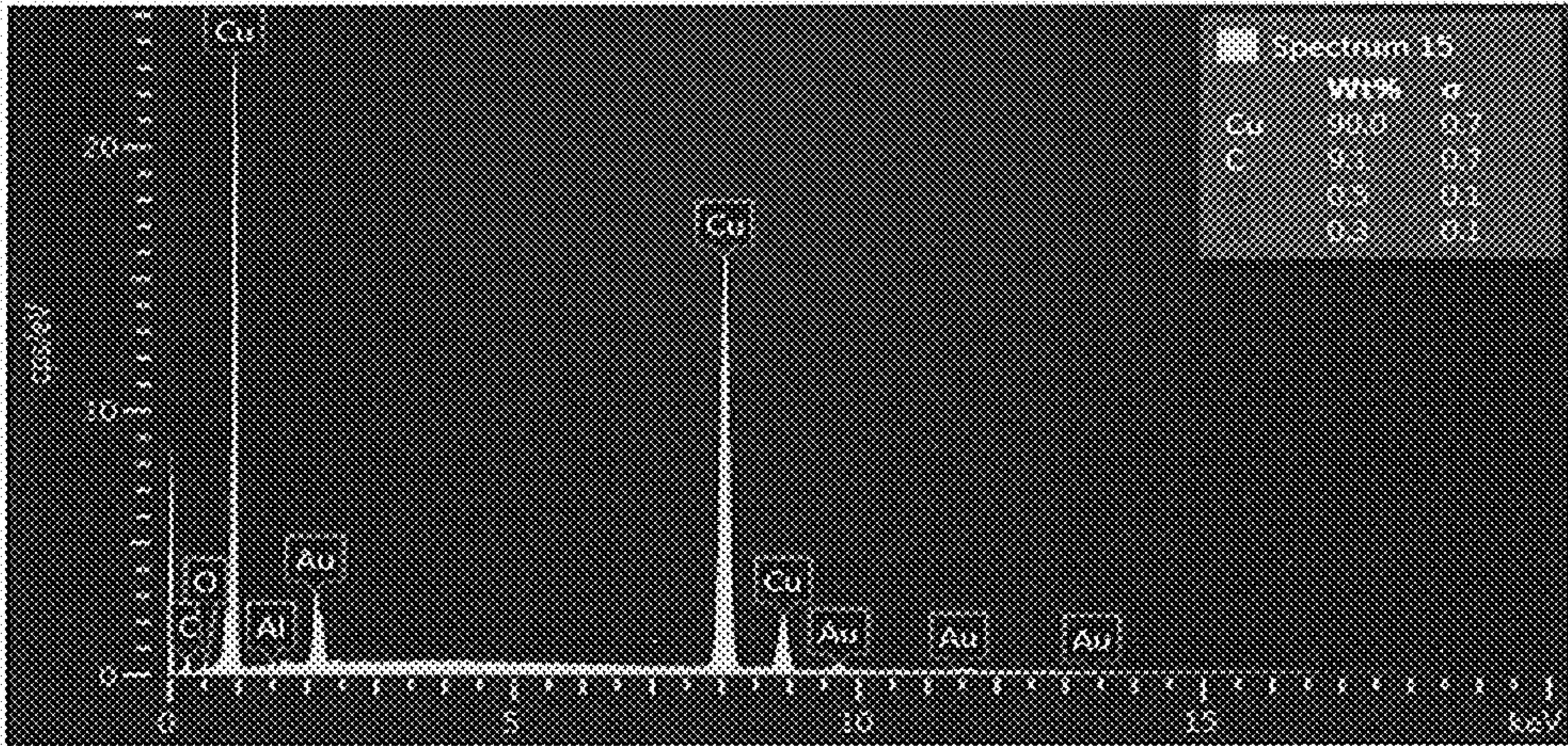


FIGURE 2

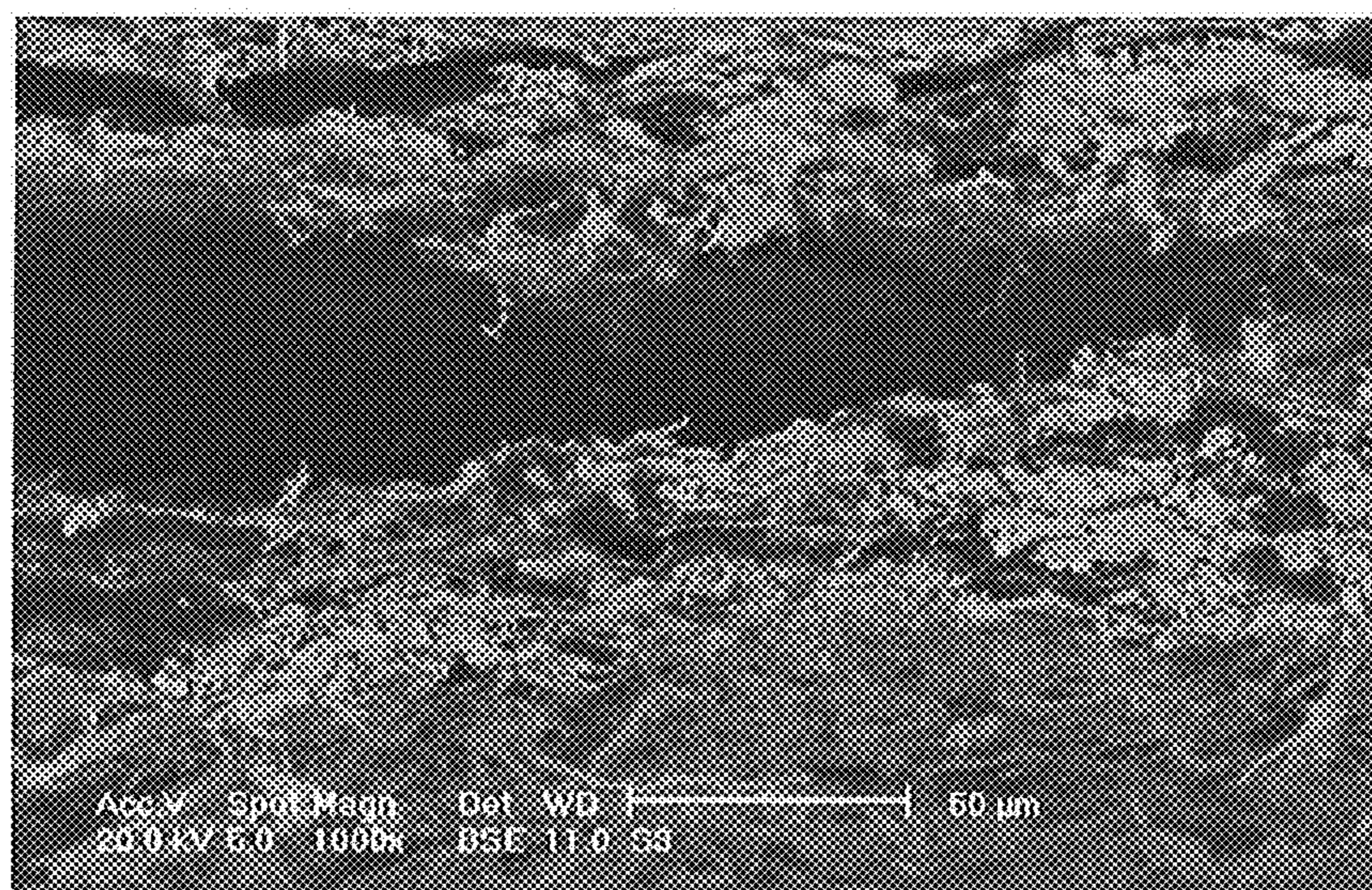


FIGURE 3

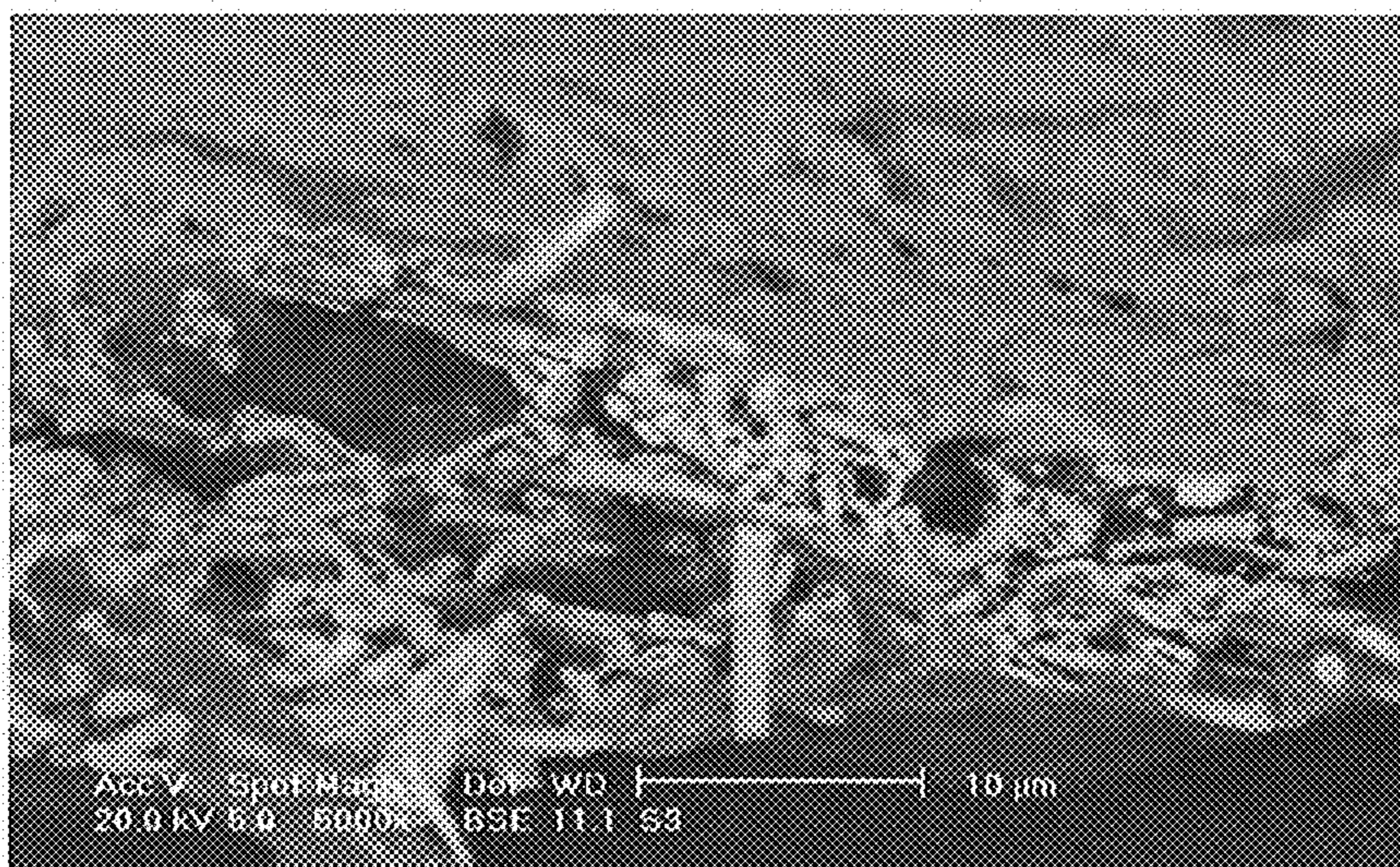


FIGURE 4

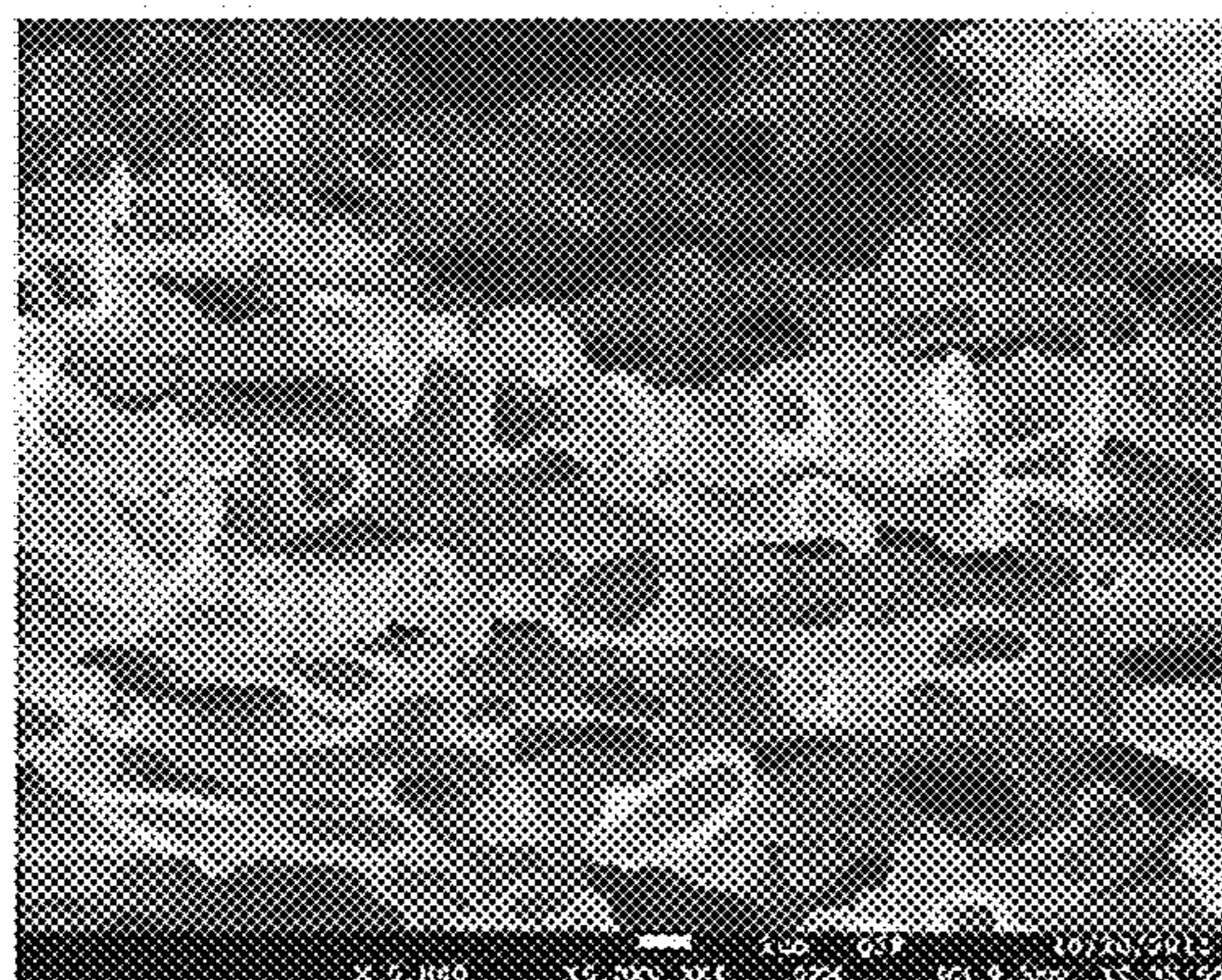


FIGURE 5

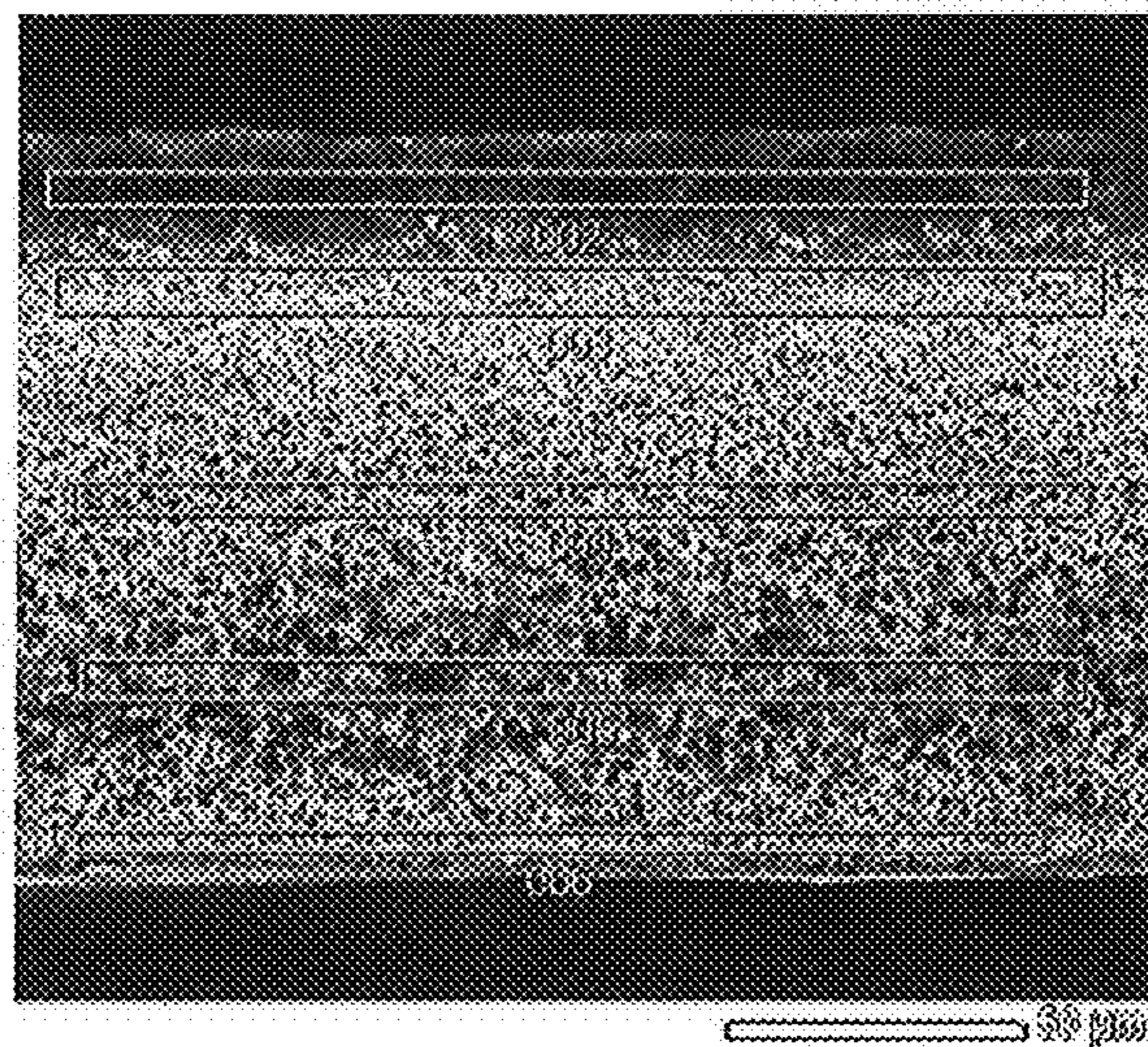


FIGURE 6

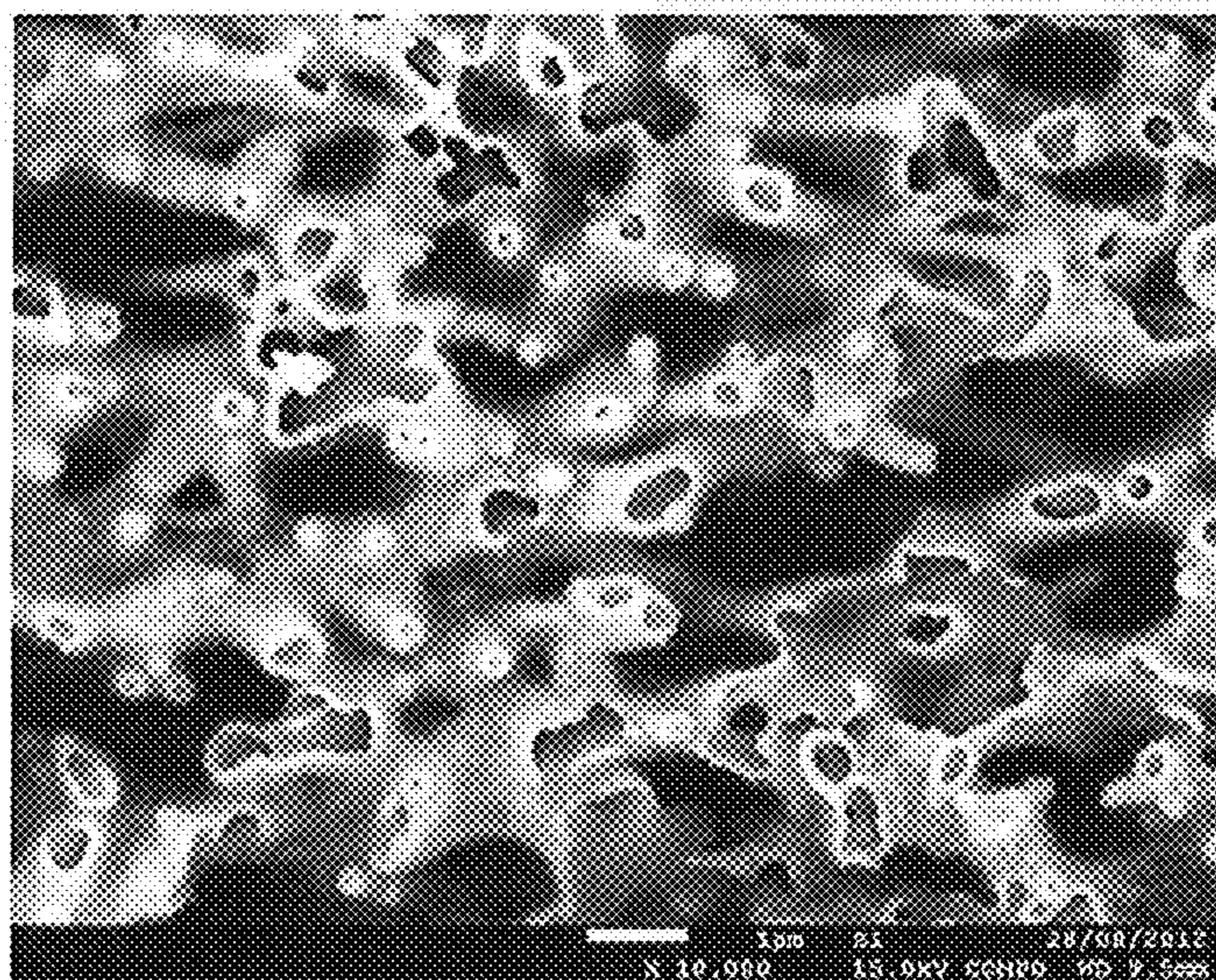


FIGURE 7

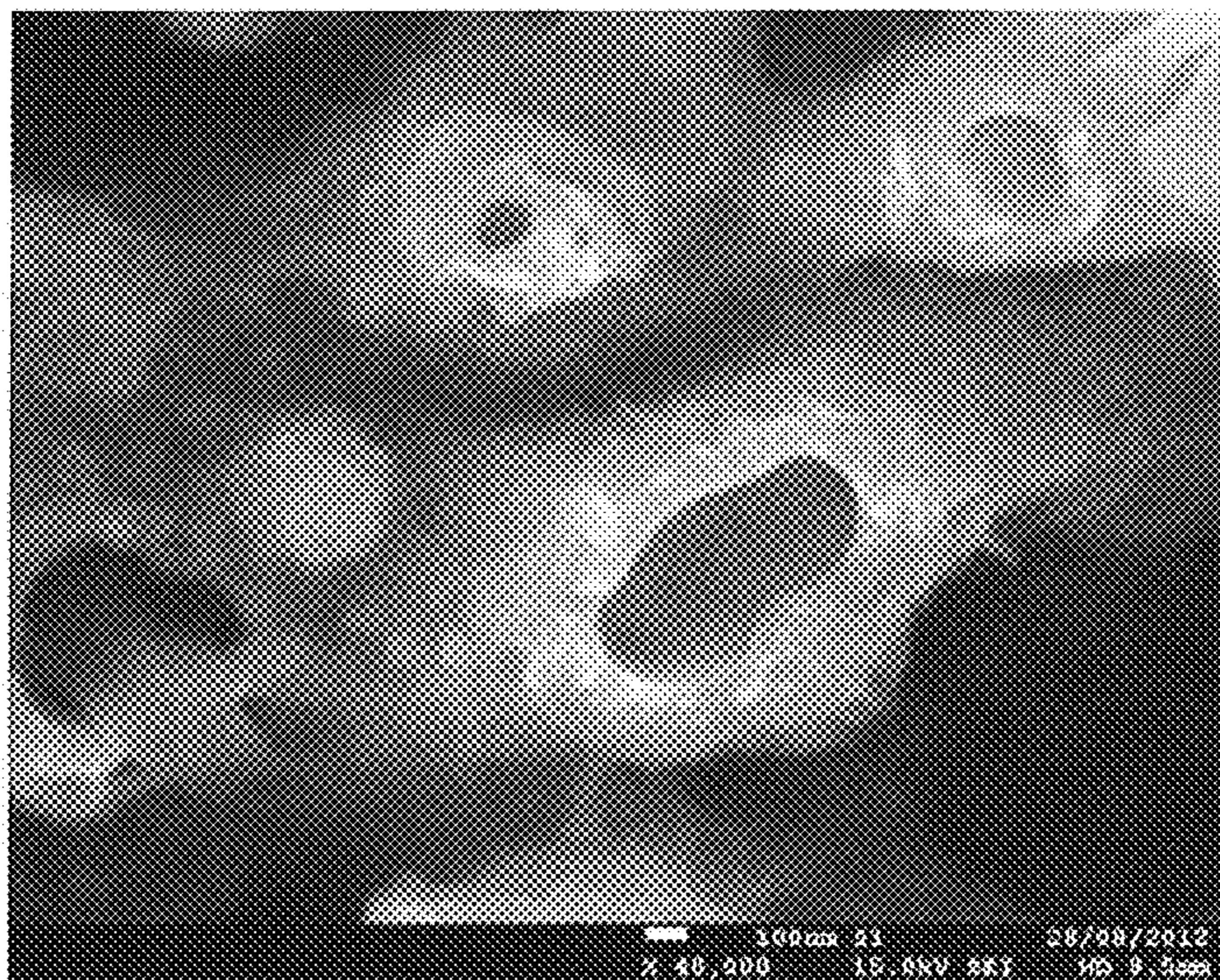


FIGURE 8

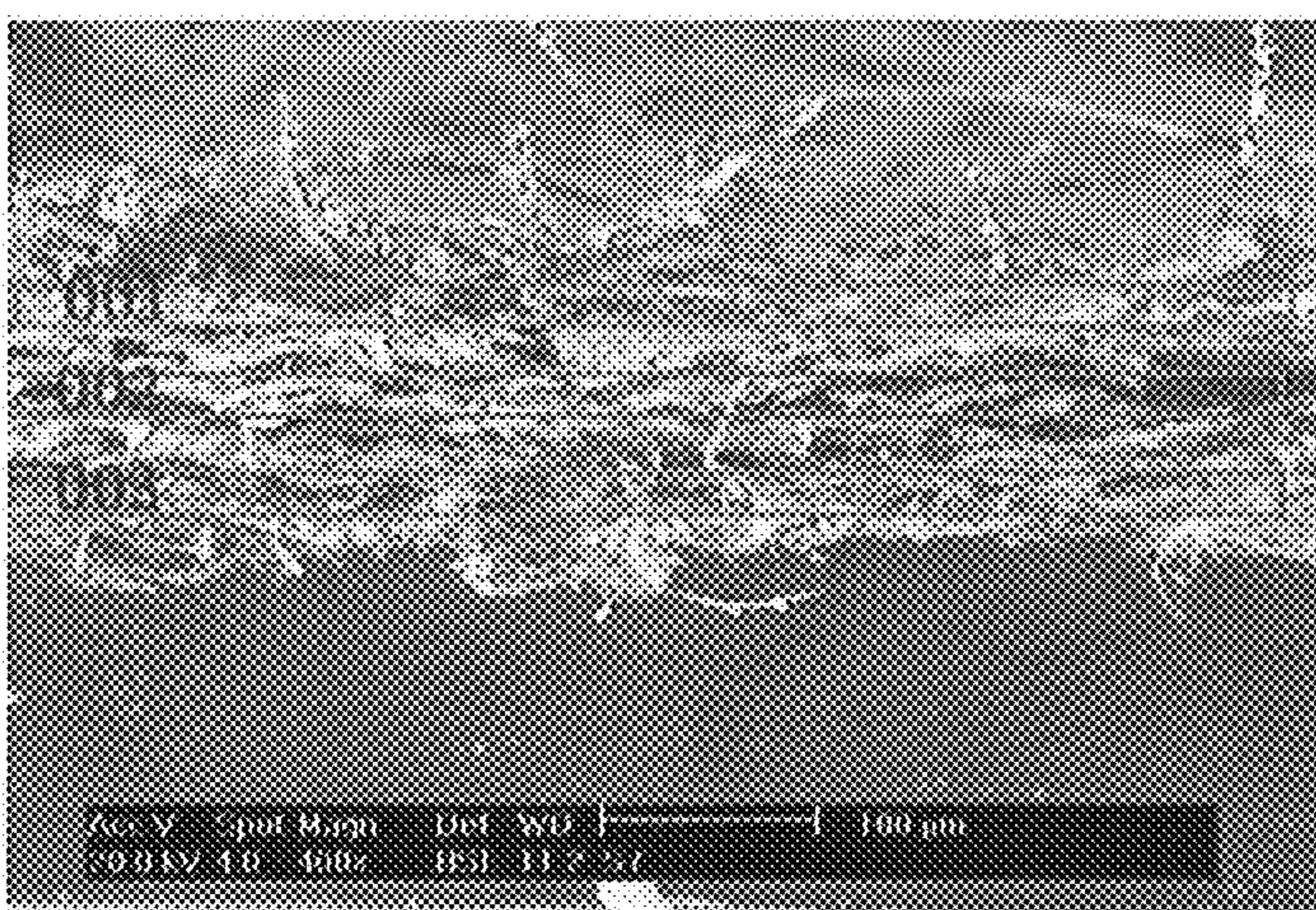


FIGURE 9

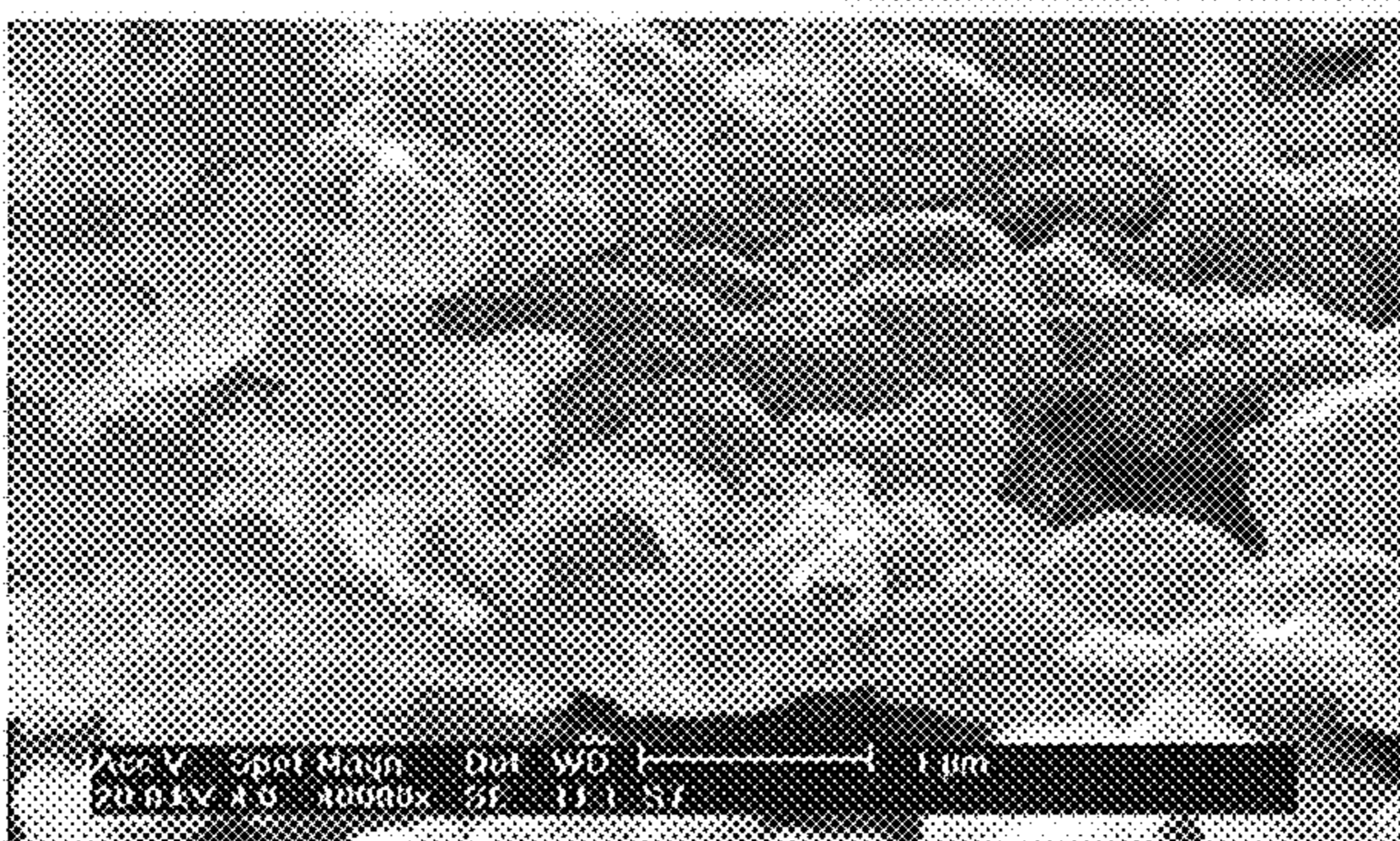


FIGURE 10

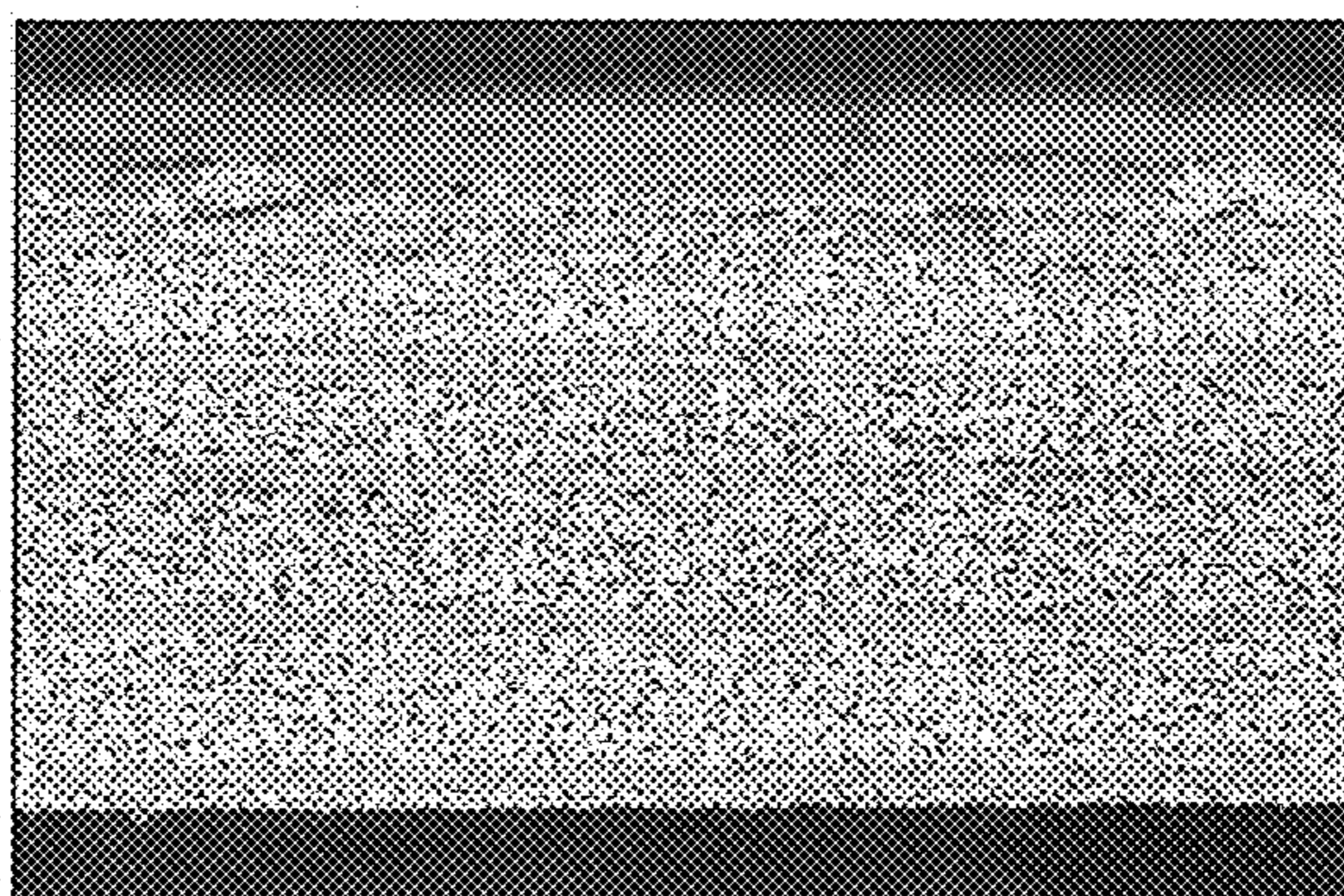


FIGURE 11

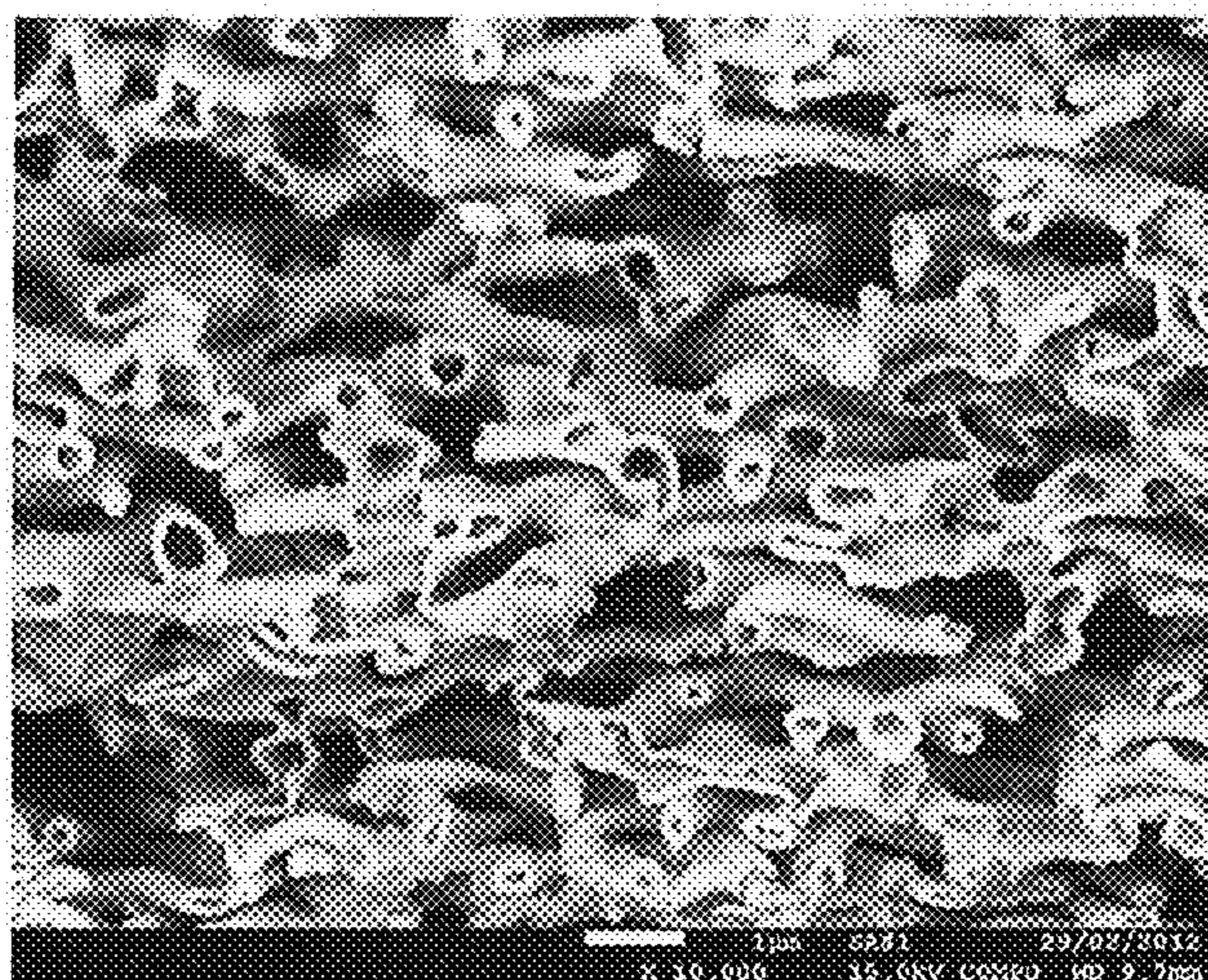


FIGURE 12

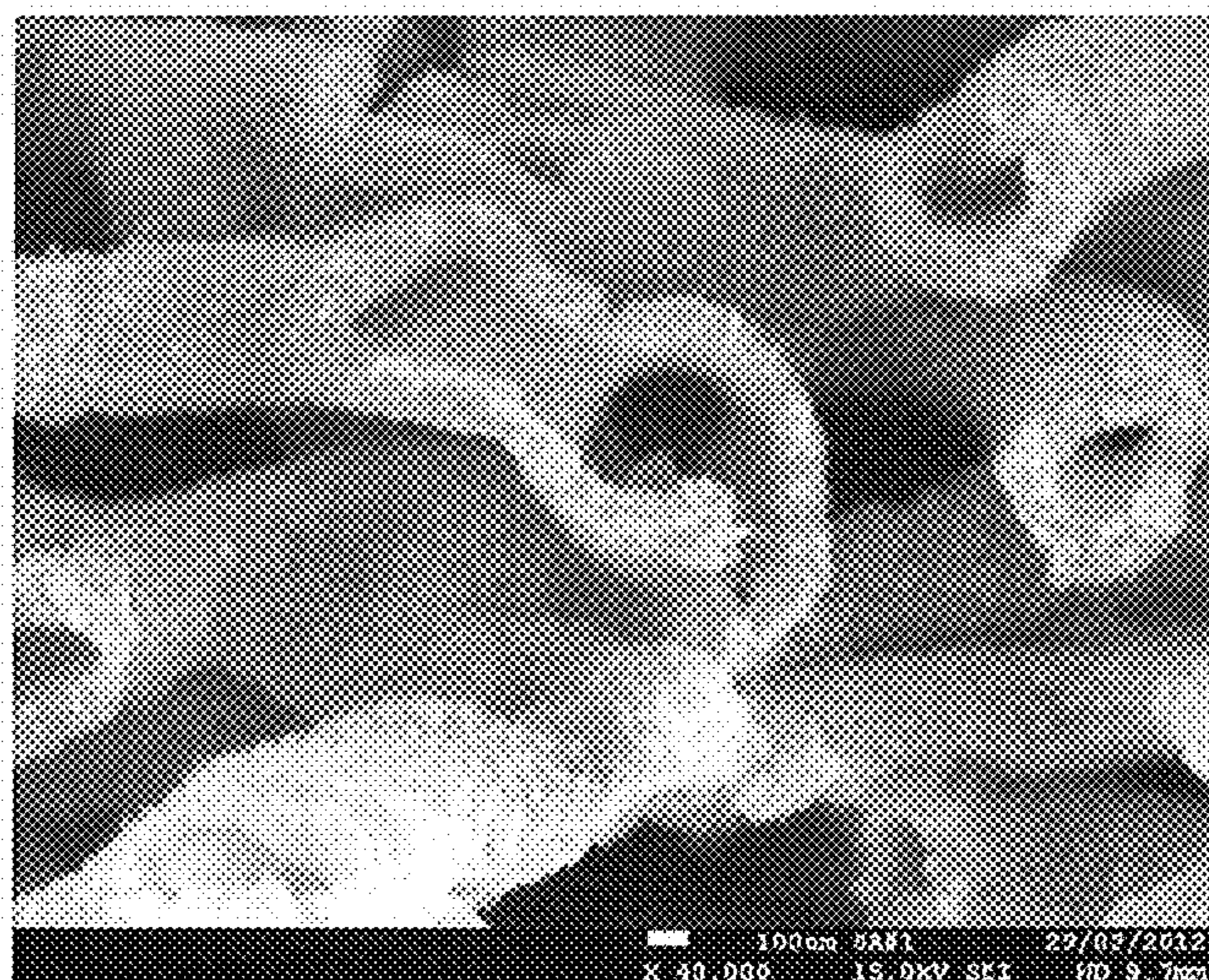


FIGURE 13

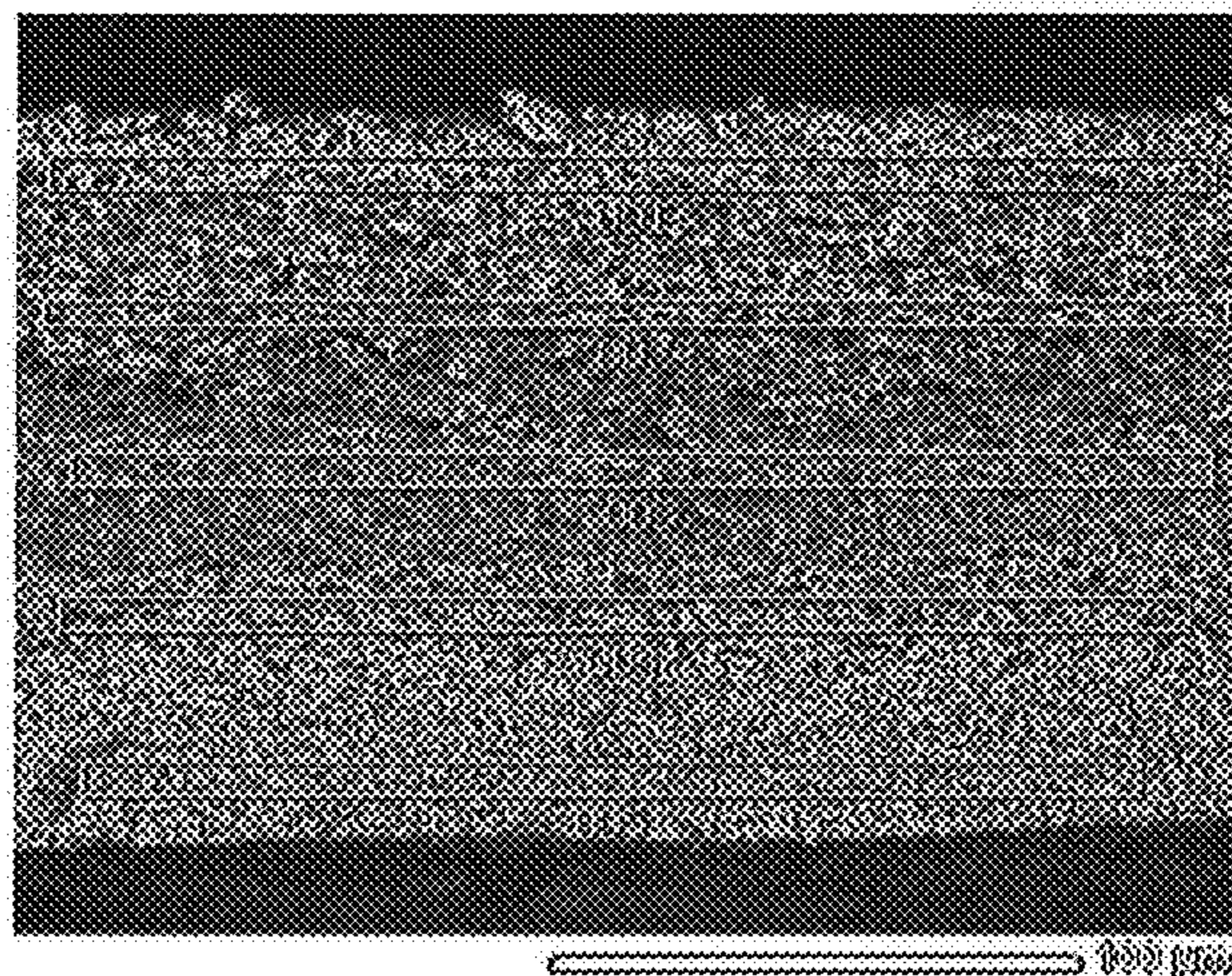


FIGURE 14

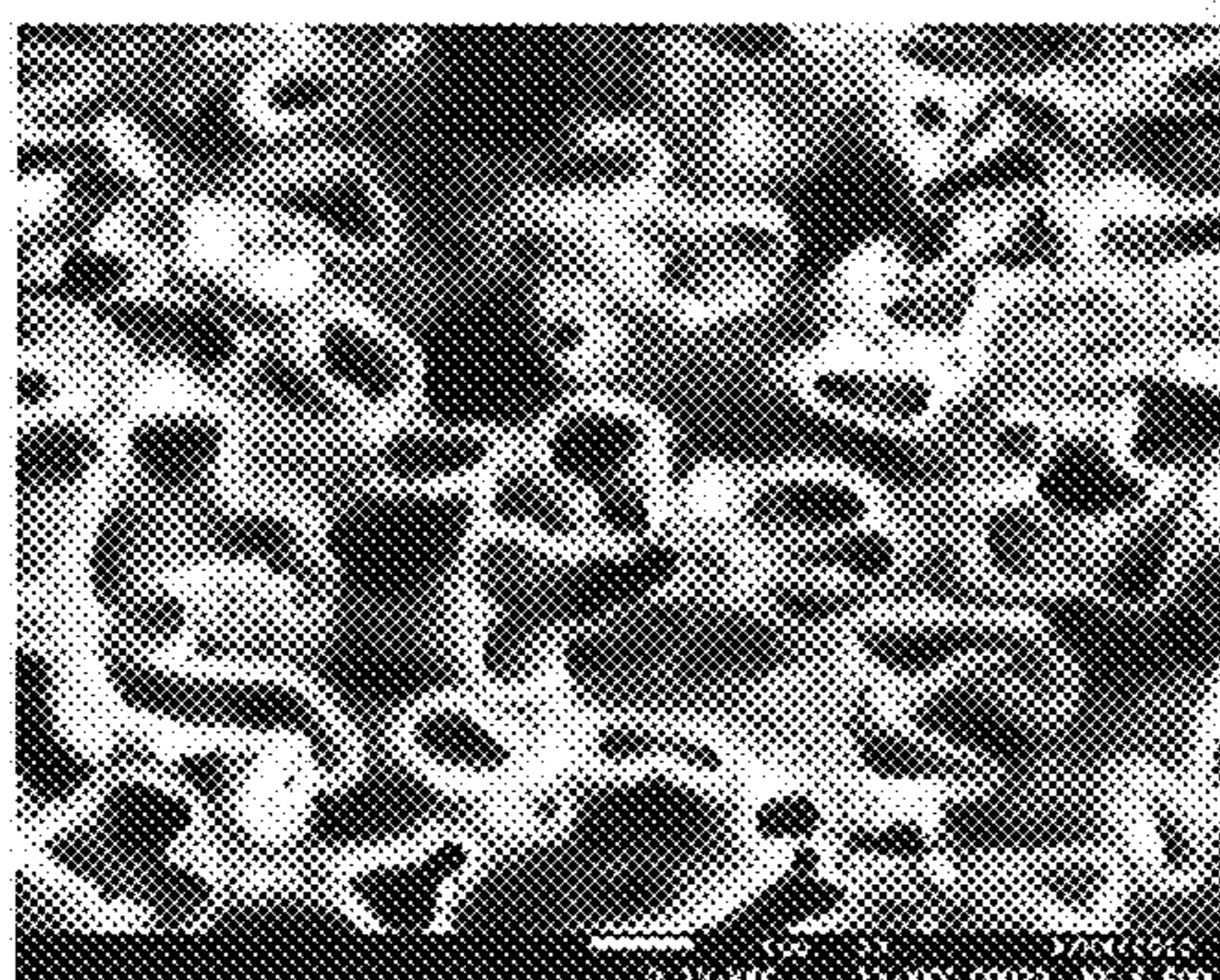


FIGURE 15

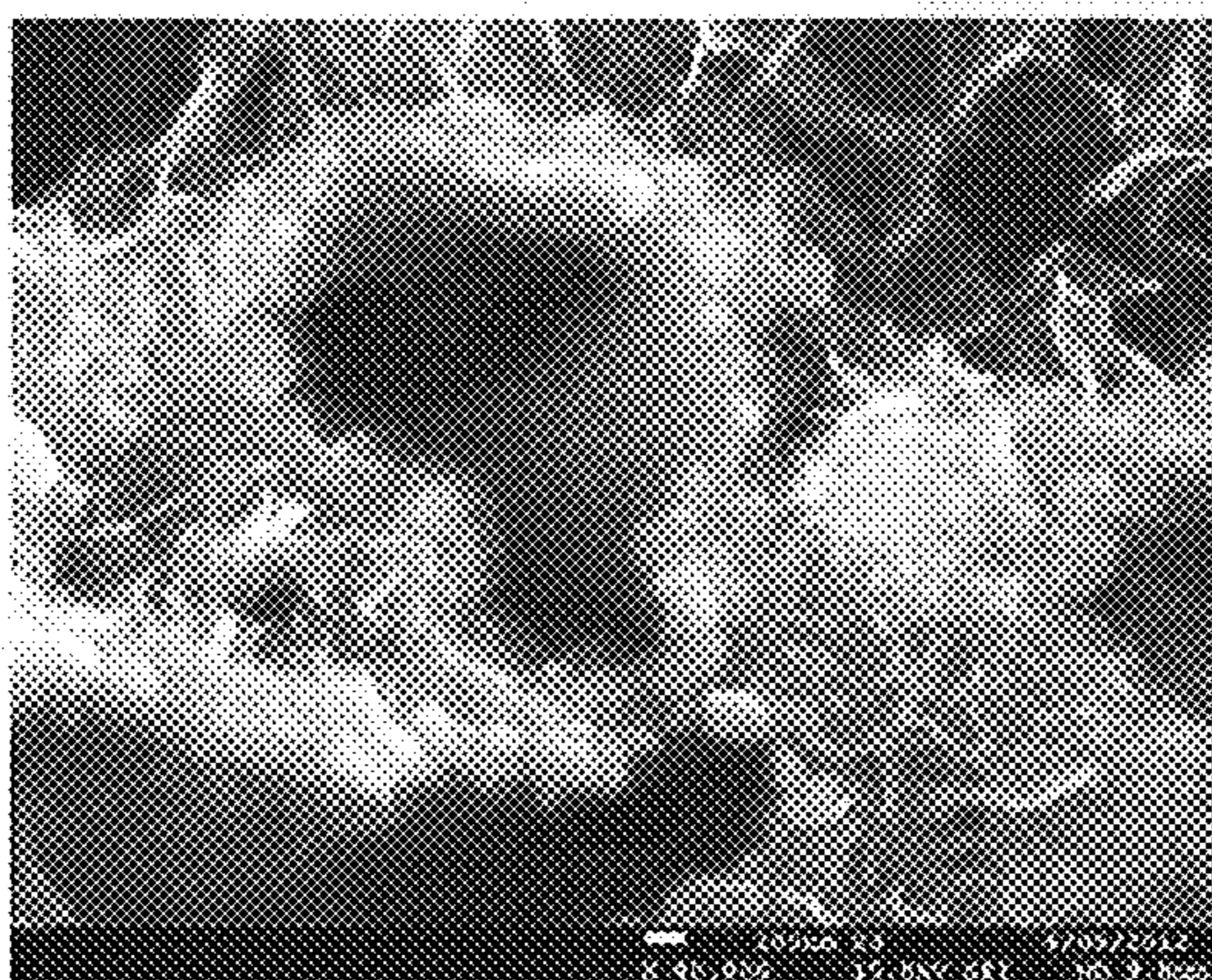


FIGURE 16

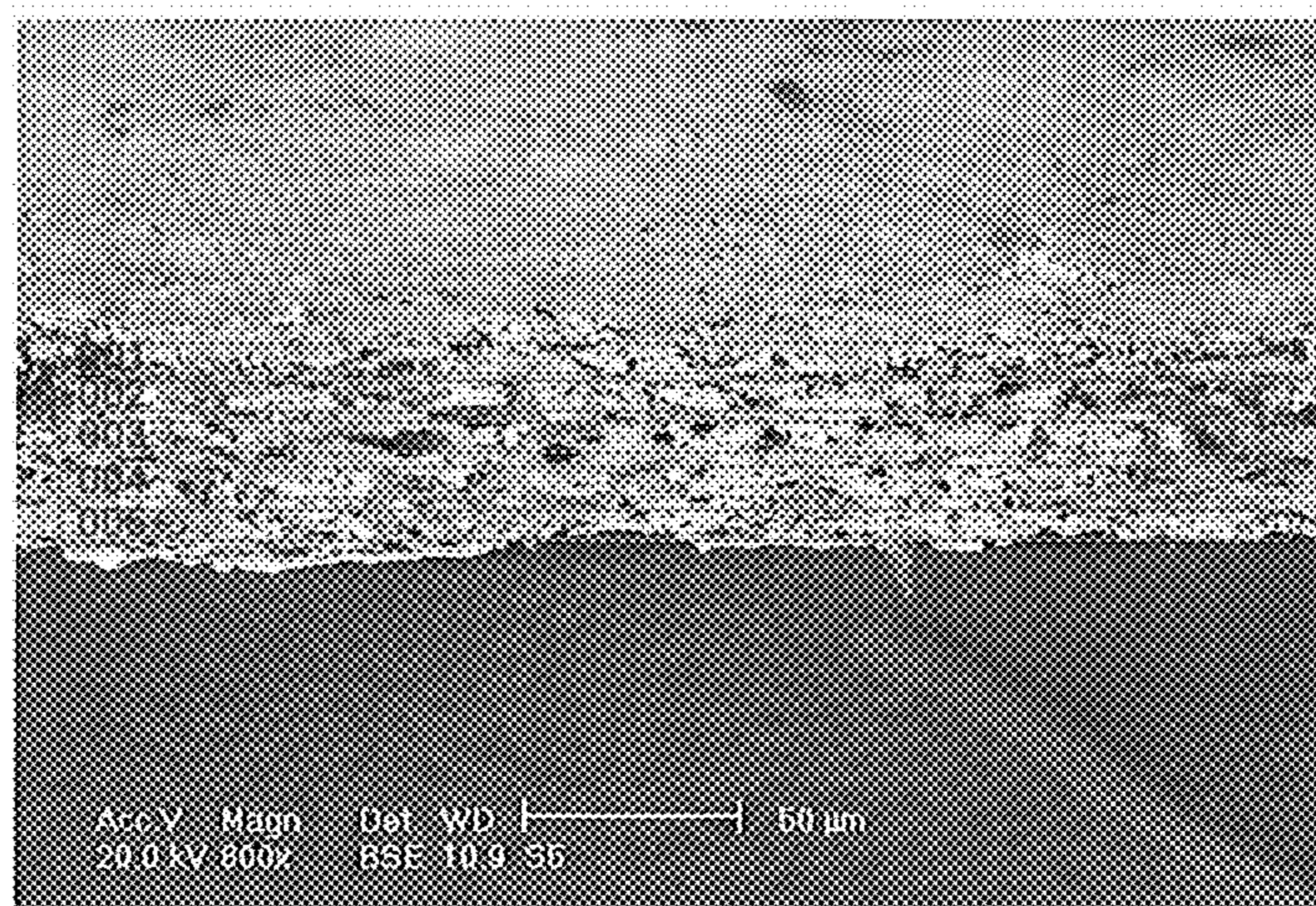


FIGURE 17

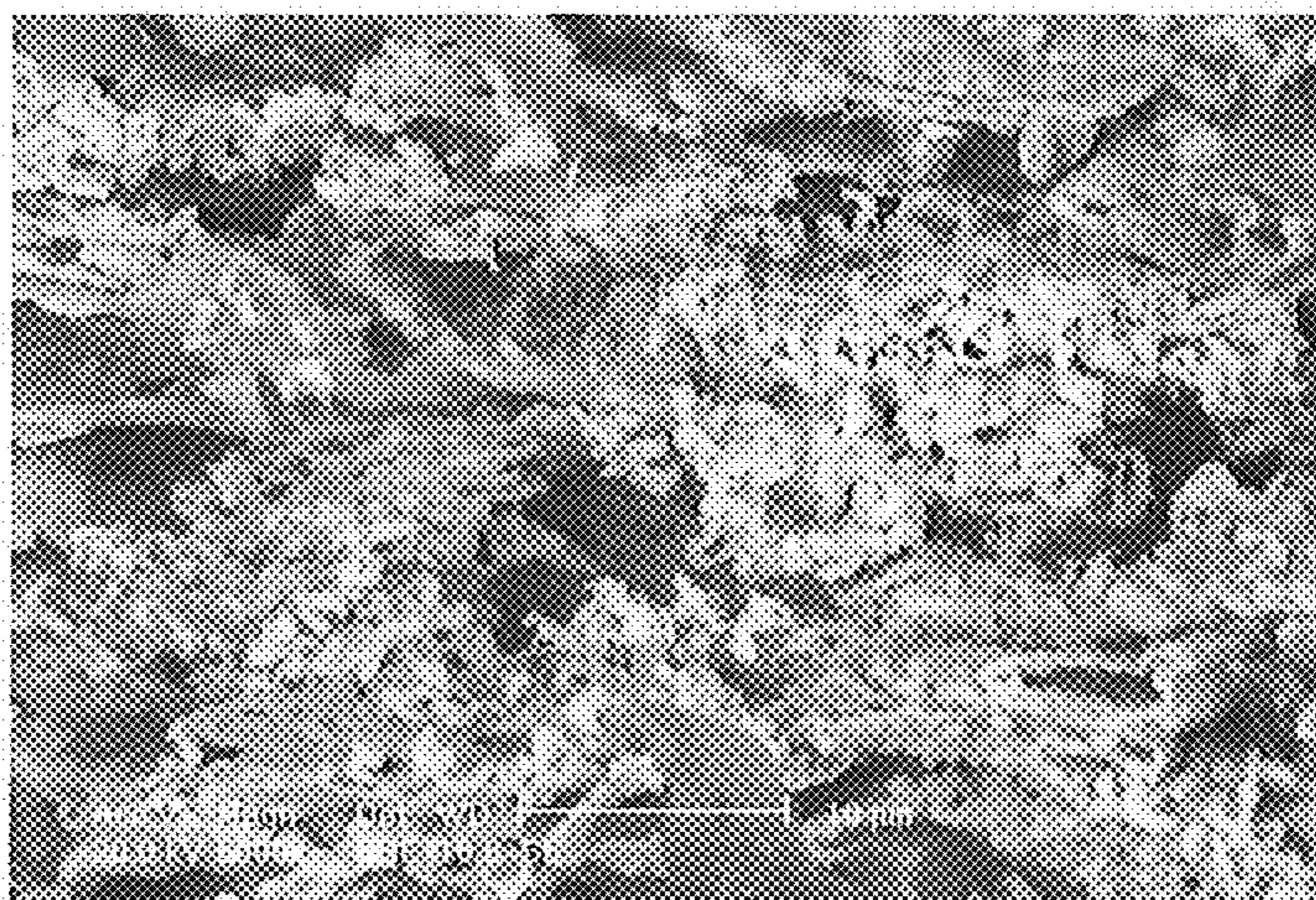


FIGURE 18

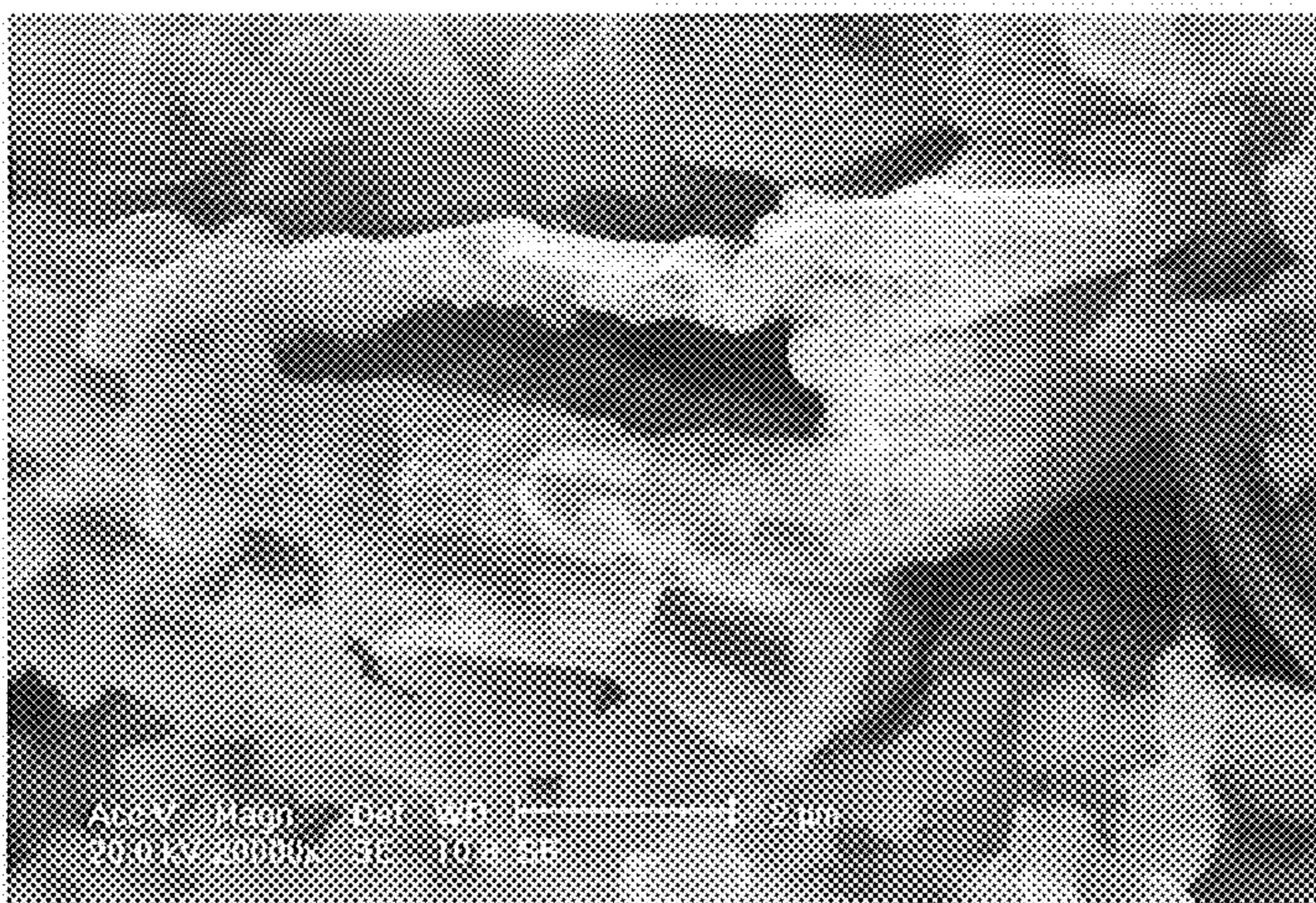


FIGURE 19

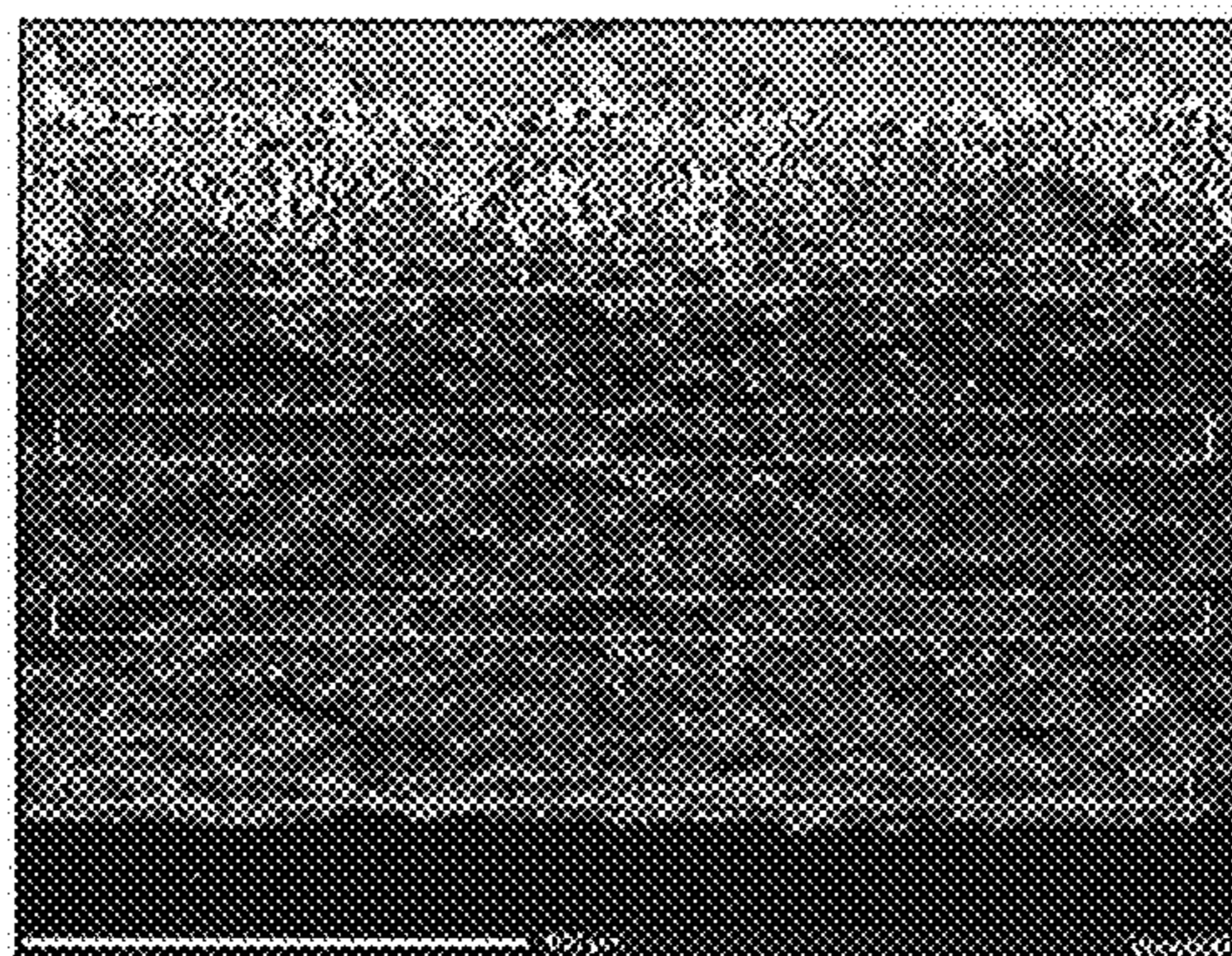


FIGURE 20

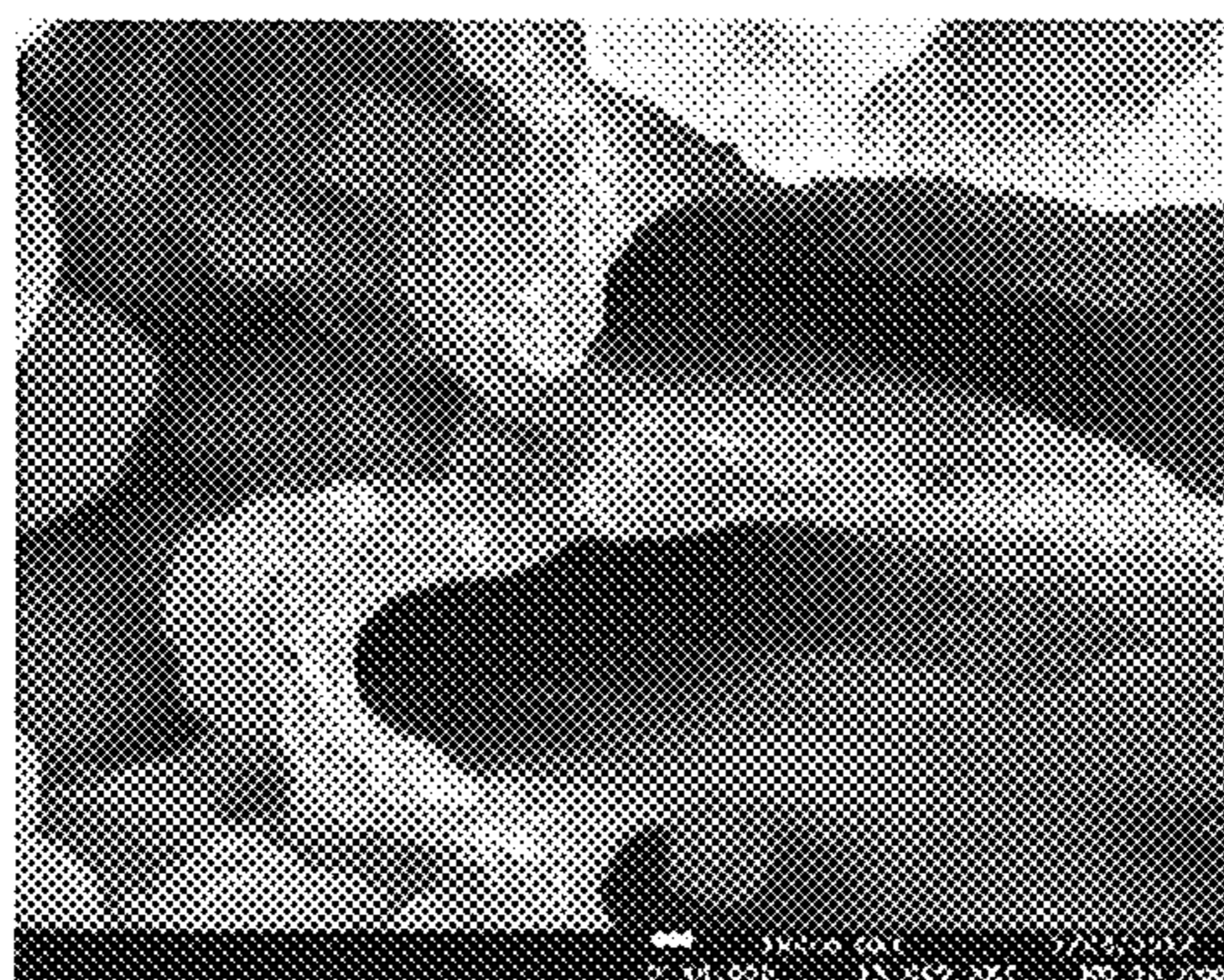


FIGURE 21

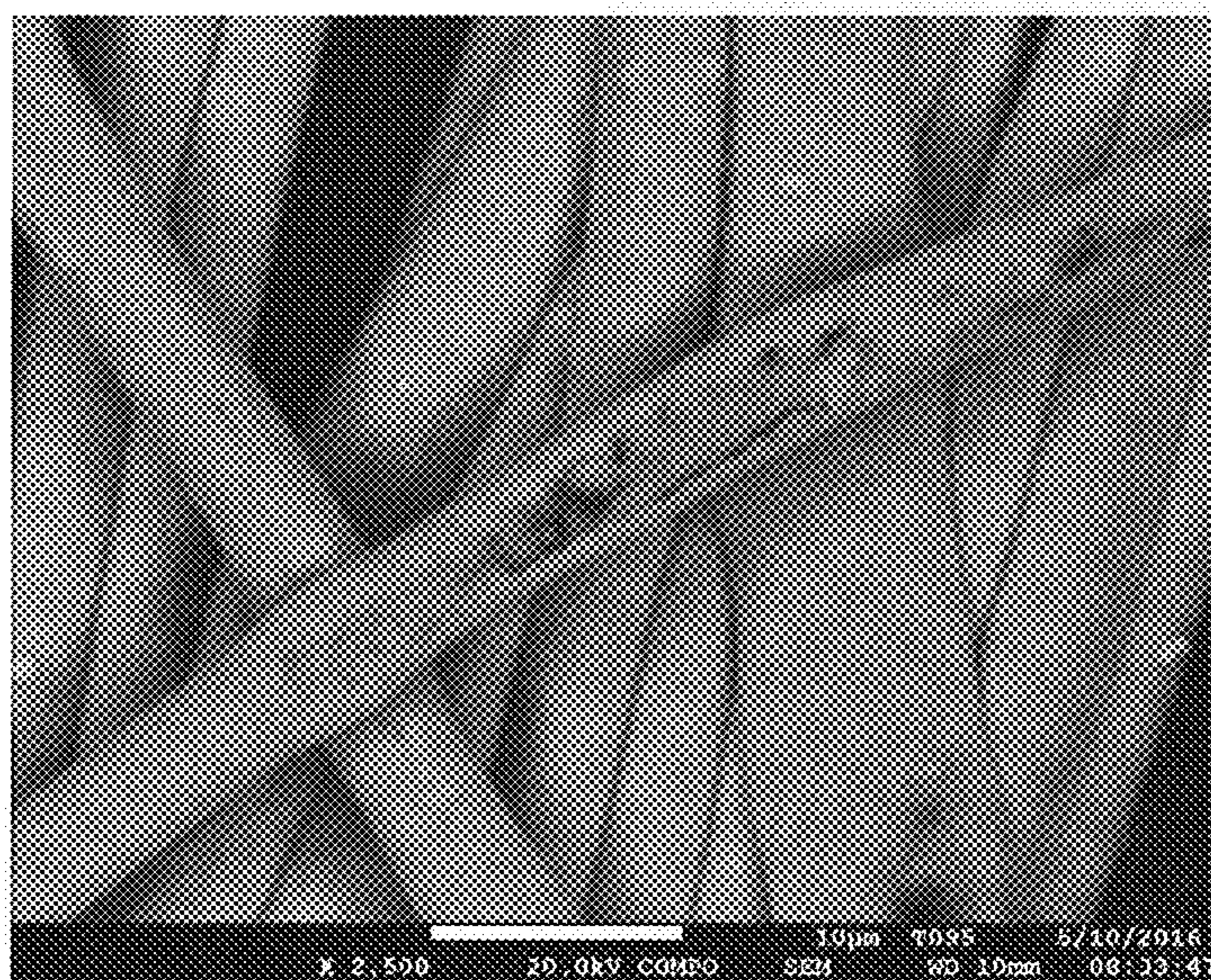


FIGURE 22

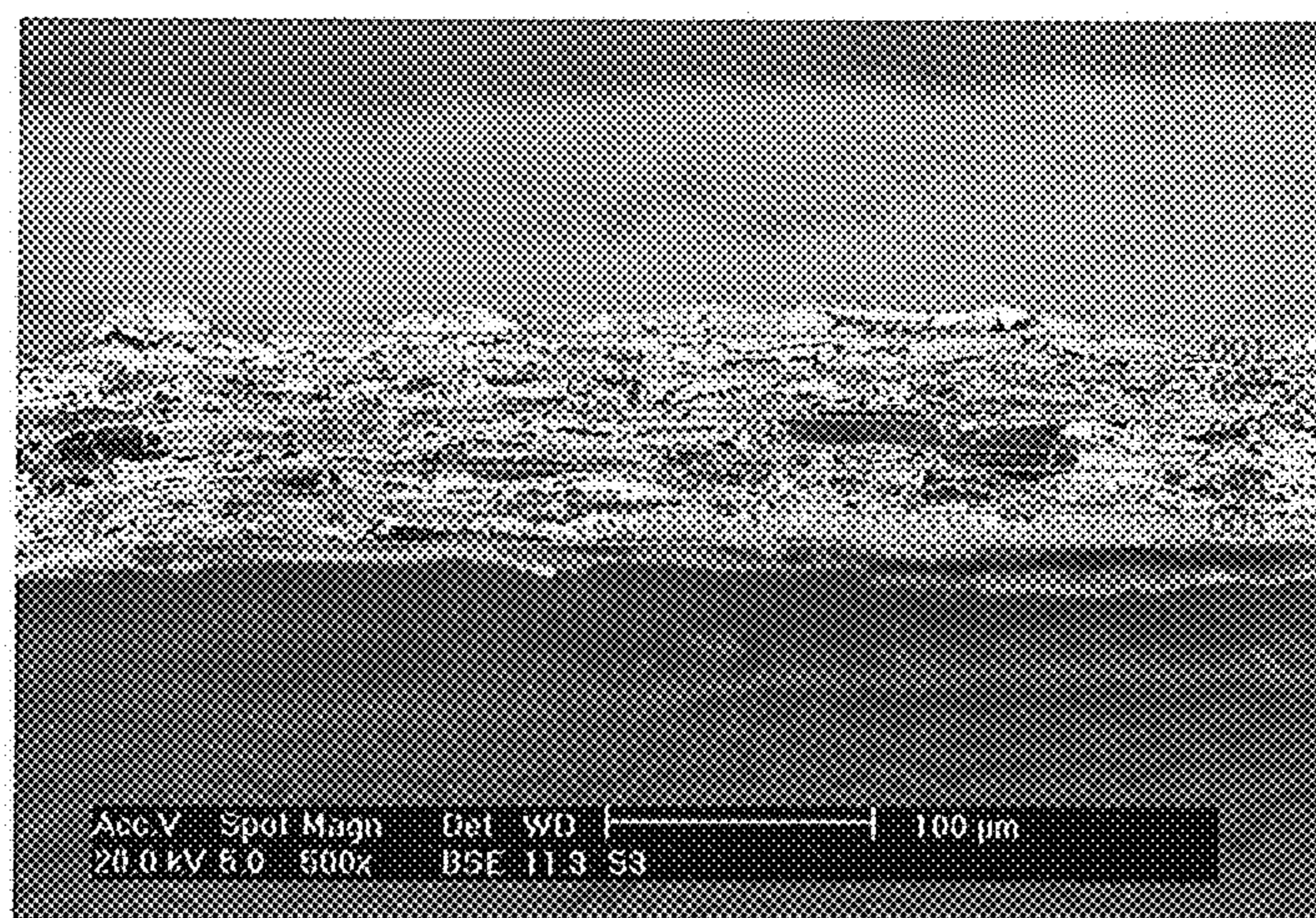


Figure 23

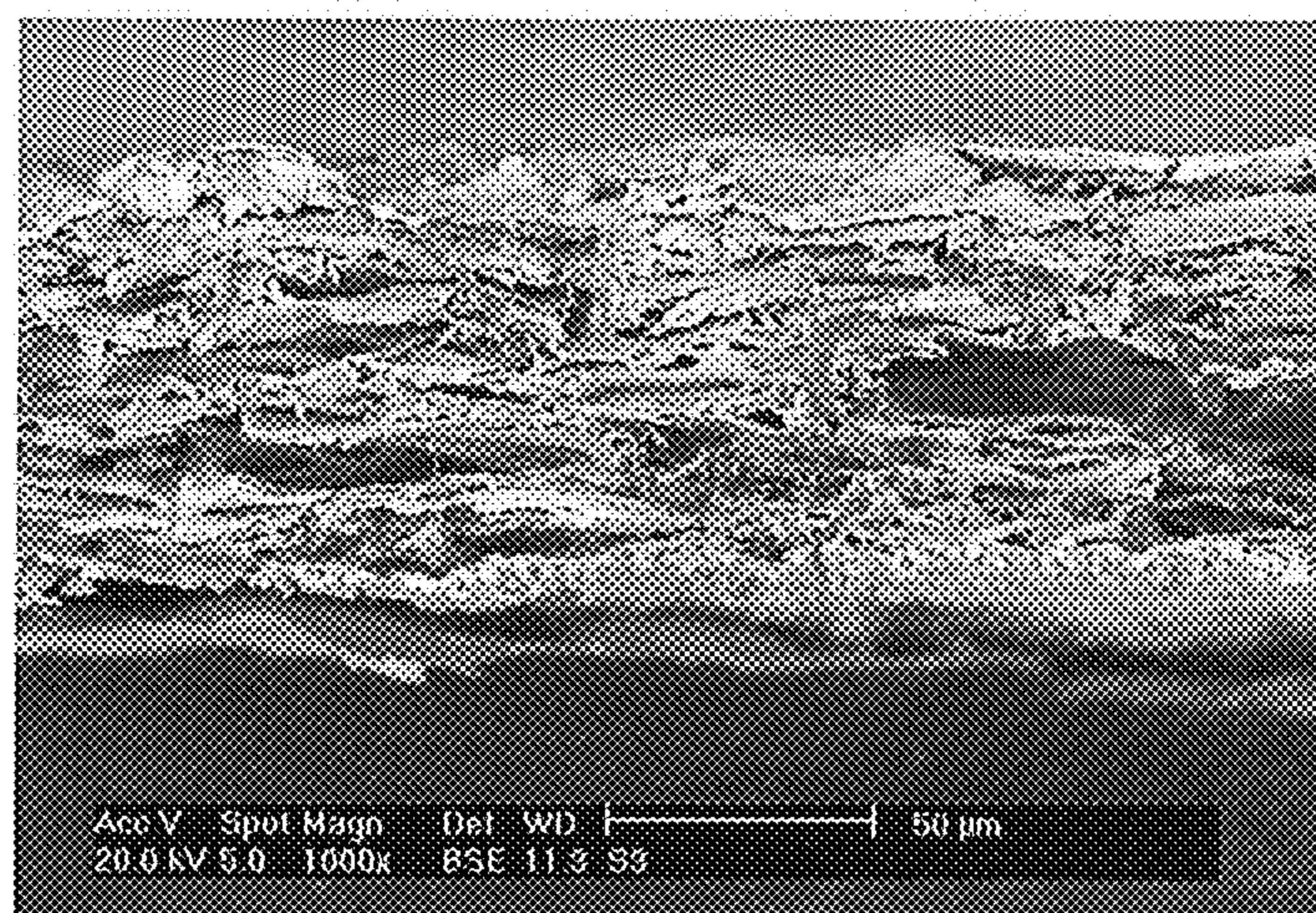


Figure 24

POROUS MATERIALS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This is a continuation-in-part of U.S. application Ser. No. 13/509,180, which is the U.S. national phase of PCT/AU2010/001511 filed Nov. 11, 2010, which claims priority to AU 2009905532 filed Nov. 11, 2009, AU 2010901022 filed Mar. 11, 2010, and AU 2010902509 filed Jun. 8, 2010, the entire respective disclosures of which are incorporated herein by reference.

FIELD OF THE INVENTION

[0002] The present invention relates to novel porous materials. In one aspect, the invention relates to porous membrane materials where specific functionalities are provided by a thin, uniform coating that is applied to an existing porous membrane material.

BACKGROUND TO THE INVENTION

[0003] Porous materials, and porous membrane materials, have wide ranging application. Materials with controlled pore structures are useful in, for example, filters for separation, water purification, air treatment, catalysis, and removal of heavy metal or biological contaminants. Materials with controllable pore sizes and conductivity are useful for applications such as batteries, supercapacitors, fuel cells and gas sensors. Pores in the nanometer size range are useful for separation processes and reactions involving biologically active molecules.

[0004] The pore structure can be critical to the performance of the porous material and/or membrane. For example, the function of filtration membranes is often to filter particles of a specific size. Usually the maximum size of particle that can pass through the membrane is specified. Thus tight control of pore structure is necessary to enable correct specification of this particle size. It may also be important to have a pore structure that achieves the required maximum particle size whilst exhibiting good permeability and that provides adequate mechanical strength.

[0005] Pore structures are critical to fluid flow through membranes. A common desire is to maximize the permeability of a membrane, which leads to lower pressure drops and therefore less energy is required to move fluid through the membrane. The permeability is a strong function of the pore structure, hence controlled and advanced pore structures are desirable.

[0006] Conducting membranes are also desired in many applications. In particular, combinations of conductivity and controlled pore structure for managing fluid flow are desired in applications such as dye-sensitized solar cells, batteries, gas sensors, fuel cells, super-capacitors, electrolyzers, photo-electrodes and some water treatment and air treatment applications. For example, many gas sensors work by using a material that changes conductivity with exposure to gas. The porous nature of the gas sensor may affect its operation by controlling how much material is exposed to the gas, and how quickly this exposure occurs. Dye-sensitized solar cells, fuel cells and batteries also require conducting porous electrodes. The porous nature of these electrodes can also be critical, as the pore structure controls movement of fluids and/or ionic species in solution. In some filtration and water treatment applications, it is important to have a conducting

membrane so that a voltage may be applied to the membrane. Permeability is again critical in terms of the pressure drop associated with flow, and associated energy requirements.

[0007] In some applications a high ratio of electrical conductivity to thermal conductivity is desired. In other words, materials with high electrical conductivity and low thermal conductivity are needed. Materials with high electrical conductivity usually exhibit high thermal conductivity. The requirement of high ratio of electrical to thermal conductivity therefore presents a significant challenge. An example of such an application is thermoelectric materials.

[0008] The field of membranes is vast and many other functionalities are required in different applications

[0009] Current membranes can be categorized into two main groups: polymer-based membranes and ceramic membranes. Whilst there are a wide variety of advanced pore structures and architectures available for polymeric membranes, these membranes are limited by their operating temperatures and resistance to certain environments. In addition, inorganic materials such as ceramics can provide functionalities that cannot be provided by polymers. For example, in many applications it would be advantageous to have conducting membranes.

[0010] Ceramic membranes exist but are much more limited in terms of available pore structures and architectures.

[0011] Polymeric membranes include filter membranes. These may be made from a variety of polymers, including cellulose, cellulose nitrate, cellulose acetate, mixed cellulose esters, nylon, PTFE (Teflon), polyether sulfones (PES), polyamides, vinyl polymers and polycarbonates. The membranes are available in a range of pore types and sizes. Typically the pore sizes are specified by the maximum particle size that can pass through the membrane. For example, a particular membrane type may be available in specified pore sizes from 0.1 μm to 10 μm . Track-etched filter membranes (typically polycarbonates) have straight cylindrical pores. However many membranes have much more complex and irregular pore structures. These include the cellulose-based filter membranes, and some nylon, PTFE and PES filter membranes.

[0012] Membranes can be made with a wide range of thicknesses, for example a few micrometers thick up to hundreds of micrometers thick or even greater into the millimeter range.

[0013] It is an object of the present invention to provide materials that significantly expand the available combinations of pore structure and functionality in membranes.

[0014] The present inventors have found that it is possible to provide desired functionalities by applying thin, uniform coatings to existing porous materials or membranes. In this way, it is possible to combine the pore structures provided by polymer-based membrane materials with functionalities provided by inorganic materials. This functionality can be added while essentially preserving, or at least altering in a controlled manner, the pore characteristics of the existing materials.

[0015] Unusual combinations of controlled pore structures and properties such as conductivity, resistance to environment and electrical conductivity to thermal conductivity ratio may be achieved by applying a thin coating of uniform thickness to an existing porous membrane. Since the coating may be very thin, the effect on pore structures may be minimized. Since the coating thickness is very controlled,

the effect on pore structures may be controlled. Also the volume fraction of coating may be controlled.

[0016] The inventors have surprisingly found that enhanced properties may be obtained by using very thin coatings and low volume fractions of solid. This is important for commercial applications.

[0017] The inventors have also surprisingly found that these enhanced properties may be achieved by coating a porous scaffold then removing the scaffold whilst maintaining reasonable properties or even enhancing properties. This removal may be achieved without excessive shrinkage in the thickness direction.

DESCRIPTION OF THE INVENTION

[0018] The inventors have surprisingly found that porous membrane materials, including polymeric filter membranes, may be coated with a uniform, thin inorganic coating which can lead to unusual features. The coating essentially preserves the original pore structure of the material. Since the coating is uniform and the thickness may be tightly controlled, the effect of the coating on the pore characteristics of the membrane, together with their associated important properties such as permeability, can be minimized or altered in a controlled manner.

[0019] In one aspect, the present invention provides a porous material comprising a porous polymeric membrane substrate having a pore size in a range from 0.1 μm to 10 μm and coated with a thin and uniform coating of one or more metals or metal alloys, the coating having a thickness that falls in the range from ~ 10 nm to ~ 1 μm , wherein the coating extends all through the thickness of the porous material and wherein the coating imparts high conductivity to the membrane such that the porous material has an equivalent conductivity of from 0.05 S/cm to 440,000 S/cm and wherein the porous material has a volume fraction of solid of less than 80%. The porous substrate may be a porous membrane substrate.

[0020] In a second aspect, the present invention provides a porous material comprising a porous polymeric membrane substrate having a pore size in a range from 0.1 μm to 10 μm and coated with a thin, uniform coating of one or more metals or metal alloys, the coating having a thickness that falls in the range from ~ 10 nm to ~ 1 μm , wherein the coating extends all through the thickness of the porous material and wherein the coating imparts high conductivity to the membrane such that the porous material has an equivalent conductivity of from 10 to 440,000 S/cm and wherein the porous material has a volume fraction of coating of less than 80%.

[0021] In some embodiments, the volume fraction of solid is less than 50%, or less than 40%, or less than 30%, or less than 25% or less than 5.5%.

[0022] In one embodiment, the porous membrane substrate comprises a filter membrane.

[0023] In one embodiment, the porous material is formed by coating a porous substrate and treating the coated material to remove the substrate and leave a porous material.

[0024] In one embodiment, the porous membrane material is formed by coating a porous membrane substrate and treating the coated material to remove the substrate and leave a porous membrane.

[0025] In one embodiment, the coating imparts high electrical conductivity to the porous material. One way of describing conductivity in porous solids is to use an 'equiva-

lent solid' conductivity. For example, if the material has a volume fraction of solid of only 20%, and the measured conductivity is x , the 'equivalent solid' conductivity would be 5 times x . Similarly, if the material has a volume fraction of solid of 50%, and the measured conductivity is y , the 'equivalent solid' conductivity would be 2 times y . This way of comparison is useful for comparing the quality of solids in structures with different volume fraction of solids. For example, comparison of the quality of the solid formed by making coatings of different thicknesses in the present invention.

[0026] In the case where the porous material is formed by a coating of material on an inert porous scaffold, it is the volume fraction of the coating material that is relevant in calculating the equivalent solid conductivity.

[0027] The concept of equivalent solid conductivity can also be applied to thermal conductivity.

[0028] In the present invention, the equivalent conductivity of the porous material may compare favorably to conductivities obtained by depositing thin films of solid materials of similar composition onto planar substrates, in particular where the thin film is of similar thickness to the coatings deposited on the porous substrates. By way of illustration, if we coat a porous substrate with a 80nm thick coating of Al-doped ZnO, a comparative thin film materials would be a solid layer of Al-doped ZnO, ~ 80 nm thick, deposited onto a flat, solid substrate. This is surprising given the tortuosity of the porous substrates, the possibilities of dead ends, and the difficulties of depositing quality material into such structures. Also surprisingly, this conductivity is retained or even enhanced following removal of the substrate, e.g. by heat treatment. For example, the equivalent conductivities of the materials of the present invention may be $\sim 1/4$ that obtained for thin films of similar composition and thickness deposited on solid substrates, or it may be $\sim 1/2$, or it may be \sim comparable to such values, or even superior. Importantly this may be achieved with low volume fractions of solid, e.g. less than 50%, or less than 40%, or less than 30%, or less than 20%.

[0029] The equivalent conductivities also compare favorably with solid (bulk) versions of materials with similar compositions. By bulk version of the materials of the present invention, we mean a solid piece of material that is of similar composition to the solid material that is present in the porous materials of the present invention. In the case where the materials of the present invention comprise a coating of material that is put onto an essentially inert scaffold/porous substrate, the relevant bulk material has similar composition to the coating. For example, if Al-doped ZnO is coated onto a porous polymer substrate according to the present invention, then an example of a bulk reference material would be a disc of Al-doped ZnO, e.g. 20mm diameter by 5mm thick. Conductivities of bulk materials are usually better than thin films. For example, the equivalent conductivities of the materials of the present invention may be $\sim 1/50^{th}$ that obtained for bulk materials of similar composition, or it may be $\sim 1/20^{th}$, or $\sim 1/10^{th}$ or $\sim 1/5^{th}$, or $1/2$ or even comparable to that obtained for bulk materials of similar composition. Again, this is surprising given the tortuosity of the porous materials, the possibility of dead ends and the difficulty of deposition into porous structures.

[0030] In some embodiments the equivalent solid conductivity of the membrane may range from ~ 0.05 S/cm to 1500 S/cm, or 10 S/cm to 1500 S/cm or 100 S/cm to 1500 S/cm.

[0031] Surprisingly these conductivities may be achieved with thin coatings, for example from ~10 nm to ~200 nm, more suitably from ~10 nm to ~100 nm, even more suitably from ~10 nm to ~50 nm, most suitably from ~10 nm to ~40 nm, ~10 nm, or 20 nm thick, or ~40 nm thick coatings. Also surprisingly, this conductivity can be achieved despite the complex solid structures of many membranes. In particular, the structures potentially represent tortuous paths, have roughness, and could consist of a number of 'dead ends'. These attributes can potentially significantly reduce conductivity.

[0032] Since the thickness of the coating is well controlled, the volume fraction of the coating is also well controlled. Also, the effect on pore structure may be minimized or at least well controlled and defined. For example, if a filter membrane's pore structure is specified as 0.2 μm , this means the largest particle that can pass through is 0.2 μm , or 200 nm. With a conductive coating of controlled thickness 20 nm, the largest particle size that can pass through is then close to 160 nm. It is possible to start with a membrane of a specified particle size, then provide a coating of a defined thickness to achieve a desired specified particle size that can pass through the porous material/membrane.

[0033] Also, by combining the surface area and volume fraction of the substrate, with the controlled coating thickness, the volume fraction of coating can be controlled accurately. An example is a filter membrane of surface area 10 m^2/g , volume fraction of solid 34%. If a flat surface is assumed, a 40 nm thick coating should lead to a volume fraction of coating of around 20%.

[0034] Surprisingly we have also found that membranes of some embodiments of the present invention exhibit a very high ratio of electrical conductivity to thermal conductivity. Materials with high electrical conductivity usually exhibit high thermal conductivity. Materials with high electrical conductivity and low thermal conductivity are, however, in demand in applications such as thermoelectric materials. Without being bound to any particular theory, the present inventors believe that the high ratios of electrical to thermal conductivities in the present materials may be due, at least in part, to phonon impediment at surfaces, probably due to surface roughness. A fine grain size may also be a contributing factor.

[0035] This ratio can be significantly higher than for bulk materials of similar composition. For example, the ratio can be 2 \times higher, or 5 \times higher, or 10 \times higher or 20 \times higher than reported for bulk materials of similar composition.

[0036] Accordingly, in another aspect, the present invention provides a porous membrane material having a ratio of electrical conductivity to thermal conductivity at least 2 \times higher, or 5 \times higher, or 10 \times higher or 20 \times higher than reported for bulk materials of similar composition. Accordingly, in another aspect, the present invention provides a porous membrane material having a ratio of electrical conductivity to thermal conductivity in excess of 10,000 SK/W, for example, from 10,000 to 200,000 SK/W, or from 15,000 to 100,000 SK/W, or from 20,000 to 50,000 SK/W. These figures are for values at room temperature (from ~15° C. to ~35° C.). At other temperatures the ratios may change somewhat, therefore different ranges may be relevant at other temperatures.

[0037] The inventors have also surprisingly found that the phonon thermal conductivities of the materials of the present

invention may be very low. Also, they may be much lower than for bulk materials of similar composition. For example, the phonon thermal conductivity may be less than 0.6 W/m/K, or less than 0.5, or less than 0.3, or less than 0.2. Correspondingly this value may be comparable to the value for bulk materials, or it may be $\frac{1}{2}$, or $\frac{1}{4}$, or $\frac{1}{10}$ th, or $\frac{1}{20}$ th, or $\frac{1}{50}$ th of these values.

[0038] The inventors have found that conductive coatings can also lead to good thermoelectric properties, including high figures of merit, ZT. This is due to the combination of high ratios of electrical to thermal conductivities and reasonable Seebeck coefficients. This ZT may be comparable or higher than ZTs for bulk materials of similar composition. Importantly these ZTs may be obtained with low volume fractions of solid.

[0039] Accordingly, in another aspect, the present invention provides a porous material, such as a porous membrane material, having a ZT comparable to that of bulk materials of similar composition, or greater than 1.2 \times higher than comparable bulk materials, or greater than 2 \times higher, or greater than 3 times higher, or greater than 5 times higher, or greater than 10 \times higher. This may be achieved with low volume fractions of solid (v_f solid), for example less than 50% v_f solid, or less than 40%, or less than 30%, or less than 20% v_f solid.

[0040] Surprisingly, the inventors have found that these properties related to conductivity can be attained using low volume fractions of solid. In prior art, porous ceramics with low volume fractions of solid lead to very low electrical conductivities. Thus the properties of such porous ceramics related to electrical conductivity, e.g. thermoelectric performance, would be expected to be poor. However the present inventors have found that good properties related to electrical conductivity, including thermoelectric performance, may be achieved whilst using low volume fractions of solid. For example the properties may be obtained with a volume fraction of solid less than 80%, or less than 50%, or less than 40%, or less than 30%, or less than 20%.

[0041] For conducting coatings, any coating providing suitable conductivity may be used. Examples include one or more metals or metal alloys is selected from the group consisting of copper, tin, nickel, iron, aluminium, titanium, cobalt, zinc, manganese, silver, gold, antimony, cadmium, tellurium, bismuth, platinum, palladium, ruthenium, rhodium, chromium, magnesium, calcium, beryllium, zirconium, molybdenum, lead, vanadium, potassium, niobium, cadmium, iridium, osmium, rhenium, indium, gallium, germanium, thallium, selenium and alloys thereof, and alloys comprising SnNi, SnFe, SnBi, SnSe, SnSb, SnSbNi, SnSbCo, CuSn, CuZn, or metals such as copper, tin, nickel, iron, aluminium, titanium, zinc, manganese, silver, gold, and alloys of these, Mg_2Si , MnSn, MgSn, alloys based on the combination of titanium and aluminum.

[0042] In another aspect of the present invention, the coating may comprise one or more metal phosphides. In this aspect, the present invention provides a porous material comprising a porous polymeric membrane substrate having a pore size in a range from 0.1 μm to 10 μm and coated with a thin and uniform coating of one or more metal phosphides, the coating having a thickness that falls in the range from ~10 nm to ~1 μm , wherein the coating extends all through the thickness of the porous material and wherein the coating imparts high conductivity to the membrane such that the porous material has an equivalent conductivity of from 0.05

S/cm to 440,000 S/cm and wherein the porous material has a volume fraction of solid of less than 80%. The metal phosphides may be selected from one or more of phosphides: including but not limited to copper phosphide, iron phosphide, tin phosphide, nickel phosphide, and other phosphides included in the metals set out above. Other features of the first aspect of the present invention may also be included in this aspect of the present invention.

[0043] A conductive carbon-based material may also be utilized. This list is not considered exhaustive.

[0044] In some instances, the material needs to be heat treated or annealed after deposition to activate the dopants. Also, post heat treatment may be used to improve the material, for example by reducing defects, growing grains, activating dopants etc.

[0045] The inventors have also found that by using thin, uniform coatings, the resistance of the membranes to environmental conditions such as temperature and chemicals such as solvents, can be improved, whilst maintaining control over the pore characteristics of the membranes. Again, the use of thin, uniform coatings enables this resistance to be achieved whilst essentially preserving the pore structure of the material, or at least altering the pore structure in a controlled manner.

[0046] Surprisingly the inventors have found that this resistance to environmental factors such as temperature and chemicals (for example solvents) may be achieved using very thin coatings. For example, materials with enhanced resistance to environmental factors may be achieved with a coating thickness less than 150 nm, or less than 100 nm, or less than 50 nm, or less than 30 nm, or less than 20 nm, or less than 10 nm. It is surprising that such thin coatings can infer increased resistance to environment. Coatings of such thinness, particularly when applied to polymers, would normally be expected to have defects such as pinholes or cracks that can expose the polymer to environmental substances such as air or chemicals. Also, diffusion through such thin layers could be significant.

[0047] Achieving property enhancements with such thin layers is important for several reasons:

[0048] 1) The final product can be made at significantly lower cost. This is both due to lower raw materials costs, and faster throughput through the coating process

[0049] 2) Thin coatings minimize changes to porosity, i.e. properties can be enhanced with minimal changes to the pore characteristics and associated properties such as permeability.

[0050] 3) Thin coatings minimize weight, i.e. property enhancement may be achieved without large weight gain. This could have particular relevance if the membrane material is a fabric or textile.

[0051] The materials of the present invention may also be post-treated to add additional functionality. For example, nanoparticles of material may be applied to the surface to perform specific functions. Also, coatings of other material or materials may be applied to the base structure to impart desired functionalities.

[0052] The coating may be applied by any suitable technique. In some embodiments, the coating may be applied to the surface by various means. For example, further layers may be applied by atomic layer deposition, electrodeposition, electroless deposition, hydrothermal methods, electrophoresis, photocatalytic methods, sol-gel methods, other vapor phase methods such as chemical vapor deposition,

physical vapor deposition and close-spaced sublimation. Multiple layers using one or more of these methods may also be used. It may be useful to coat the material such that the composition of the material is not uniform throughout. For example, a coating method may be used that only penetrates partway into the porous material. The coating may also be applied by sequential use of different coating methods.

[0053] In one embodiment of the present invention, the original porous substrate may be removed, after application of the coating. The inventors have surprisingly found that high conductivities may still be achieved despite application of the removal process to the material. Removal, for example, by application of heat, may be expected to be detrimental to the solid structure of the material due to forces exerted due to, for example, combustion and/or thermal expansion. Also, the inventors have found that high electrical conductivity to thermal conductivity ratios may still be maintained, even after removal of the original porous substrate. Since this removal creates extra porosity, possibly at a larger scale than the initial porosity, this removal step could potentially increase thermal conductivity by allowing heat transfer via air or other gases. This heat transfer could also or alternatively be via conduction or convection in the gas. The inventors have surprisingly found that the solid part of the original porous substrate may be removed, without greatly increasing the thermal conductivity, or at least without greatly decreasing the ratio of electrical conductivity to thermal conductivity.

[0054] In one embodiment of the present invention, the original porous scaffold may be removed whilst maintaining reasonable compressive strength. For example, the material may have a compressive strength of greater than 1 MPa, or greater than 2 MPa, or greater than 10 MPa, or greater than 20 MPa. Surprisingly these compressive strengths may be achieved with low volume fractions of solid, for example less than 50% v_f solid, or less than 40%, or less than 30%, or less than 20% v_f solid.

[0055] In one embodiment of the present invention, the original porous scaffold may be removed without causing significant shrinkage. For example, the thickness of the material after removal of the scaffold may be within 20% of the original thickness, or within 10%, or within 5%, or within 2%.

[0056] In another embodiment of the present invention, the coating may be comprised of multiple layers. Said multiple layers may be deposited using one, or more than one, deposition technique.

[0057] In another embodiment of the present invention, the coating is comprised of nanolayers of material. The inventors have found that nanolayered materials may be deposited that exhibit good conductivity and good values of electrical to thermal conductivity.

[0058] In one embodiment, the coating is applied to the substrate by an ALD process. An ALD process requires the following steps to form a 'cycle'.

[0059] 1. Dosing of metal precursor, during which a layer of metal precursor reacts with the surface and is attached to the surface. Additional precursor molecules cannot react with precursor molecules already attached to the surface, so the process is self-limiting.

[0060] 2. Inert gas purge that removes both unreacted precursor molecules, and reaction products from the reaction of precursor molecules with the surface.

[0061] 3. Dosing of a reactant, which reacts with the metal precursor molecules that are attached on the surface. The surface can then react with another dose of metal precursor.

[0062] 4. Inert gas purge that removes the reactant.

[0063] This cycle may be repeated any number of times in order to build up a coating of controlled thickness.

[0064] However, ALD on porous structures, particularly structures with high effective pore aspect ratios (in a cylindrical pore, the aspect ratio is length divided by diameter) has in the past proved problematical. In particular, complex structures with tortuous paths, such as those found in many polymeric filter membranes, can significantly inhibit gaseous flow, thereby creating problems for ALD. Also, deposition on polymeric materials can be difficult due to problems with nucleation.

[0065] The inventors have found that these problems can be overcome to provide the materials of the present invention.

[0066] In another aspect, the present invention provides a method for forming a porous material comprising providing a porous substrate material and applying a thin uniform coating to the porous structure material.

[0067] In some embodiments of the method of the present invention, the porous material is made by applying a thin, uniform coating to a porous substrate material and subsequently removing the porous substrate material. The porous substrate material may be removed, for example, by heat treatment or by chemical treatment. The heat treatment or chemical treatment desirably removes the substrate material without unduly affecting the coating material. Surprisingly it has been found that the polymeric substrate can be removed without unduly affecting the material in an adverse manner, and in fact the removal process may actually enhance some properties. Removal of such material may normally affect the structural integrity of the structure and/or adversely affect the deposited solid in a chemical way.

[0068] In another embodiment of the method of the present invention, the porous layer may first be applied to a substrate. The thin coating is then applied to the porous layer, while the porous layer is on the substrate.

[0069] Throughout this specification, where reference is made to a comparison or ratio of properties referenced to the properties of comparable bulk materials or bulk materials of similar composition, it is meant the properties of the porous material are compared to a bulk material of similar composition to the solid part of the porous material, where the bulk material is a piece of solid material, or nearly solid material, that has dimensions in the millimeter range or larger. For the case where the porous material is comprised of a coating of material applied to an essentially inert substrate, the bulk material is of similar composition to the composition of the coating material, i.e. the composition of the inert substrate is not relevant.

[0070] Where reference is made to a comparison or ratio of properties referenced to the properties of comparable thin-film materials or thin-film materials of similar composition, it is meant that the properties of the porous material are compared to a thin-film of solid material of similar composition to the solid part of the porous material, deposited onto an essentially flat, solid substrate. For the case where the porous material is comprised of a coating of material applied to an essentially inert substrate, the thin-film material is of similar composition to the composition of the coating material, i.e. the composition of the inert sub-

strate is not relevant, and the thickness of the thin-film material is similar to the coating thickness.

[0071] The porous substrate used in the present invention is suitably a porous membrane. Such porous membranes include polymeric filter membranes, filter papers, track-etched membranes, sintered ceramic membranes, other ceramic membranes, porous metallic membranes, aerogel membranes or xerogel membranes. The membranes may have a wide range of thicknesses, from the micrometre range to the millimeter range.

BRIEF DESCRIPTION OF THE DRAWINGS

[0072] The patent or application file contains at least one drawing executed in color. Copies of this patent or patent application publication with color drawings will be provided by the Office upon request and payment of the necessary fee.

[0073] FIG. 1 shows a scanning electron micrograph of the porous material obtained in Example 1;

[0074] FIG. 2 shows a compositional analysis of the porous material obtained in Example 1;

[0075] FIGS. 3 and 4 show scanning electron micrographs of the porous material obtained in Example 2;

[0076] FIG. 5 shows a scanning electron micrograph of the porous material obtained in Example 4;

[0077] FIGS. 6 to 8 show scanning electron micrographs of the coated material obtained in Example 12;

[0078] FIGS. 9 and 10 show scanning electron micrographs of the porous material obtained in Example 13;

[0079] FIGS. 11 to 13 show scanning electron micrographs of the porous material obtained in Example 14;

[0080] FIGS. 14 to 16 show scanning electron micrographs of the coated material obtained in Example 15;

[0081] FIGS. 17 to 19 show scanning electron micrographs of the porous material obtained in Example 16;

[0082] FIGS. 20 and 21 shows scanning electron micrographs of the porous material obtained in Example 18;

[0083] FIG. 22 shows a scanning electron photomicrograph of the porous material obtained in Example 20; and

[0084] FIGS. 23 and 24 shows scanning electron photomicrographs of the porous material obtained in Example 22.

[0085] In order to better understand embodiments of the present invention, the following examples are provided.

EXAMPLES

Example 1

[0086] A porous polymeric substrate, with a non-woven fibrous composite structure, which contains cellulose fibers and has a thickness of 40 μm , was pretreated with an activator pre-treatment by contacting the substrate with a solution of 0.4 g/L PdCl_2 and 10 g/L SnCl_2 in 12M HCl at a temperature of 27.5° C. for 3 minutes. A copper coating was then applied to the substrate using electroless deposition. A Macdermid Copper 85 solution, which is a proprietary commercially available electroless copper depositions solution, was used. Electroless deposition of copper took place at 45.5° C. with a contact time of 30 minutes. A copper coating was formed on the substrate. FIG. 1 shows SEM photomicrographs of the coated material. The copper coating was seen to be uniformly applied to the substrate. FIG. 2 shows a compositional analysis of the material. The material was found to contain 90 atomic % copper.

Example 2

[0087] In this example, a substrate was coated with a mixed nickel/cobalt or a nickel/cobalt alloy. A porous polymeric substrate with a non-woven fibrous composite structure, which predominantly consists out of cellulose fibers 80 μm thick, non-woven membrane reinforced through lamination to a Nylon scrim of 10-20 μm thickness was pre-treated with an activator comprising a solution of 0.4 g/L PdCl_2 and 10 g/L SnCl_2 in 12M HCl at a temperature of 27.5° C. for 3 minutes. A coating comprising nickel and cobalt was then applied by using a proprietary coating composition from Enthone that contains a Ni/Co ratio of 1:10. The substrate was contacted with this composition at 76° C. for 30 minutes, at a pH of 5.7. FIGS. 3 and 4 show SEM photomicrographs of the coated material. The nickel coating appeared to be uniformly applied to the substrate. The coating retained significant porosity.

Example 3

[0088] In this example, a substrate was coated with a nickel coating. A porous polymeric substrate with a non-woven fibrous composite structure with a thickness of 80 μm was pretreated II at a temperature of 27.5° C. for 3 minutes. A nickel coating was then applied by using electroless deposition. The substrate was contacted with a nickel electroless solution containing Ni—18.13 g/L Nickel (II) chloride, 9.06 g/L sodium citrate, 32 g/L ammonium chloride and 18.06 g/L sodium hyposphosphite. The substrate was contacted with this composition at 67-72° C. for 90 minutes, at a pH of 9. The nickel coating extends throughout substantially all of the material. The coated material has the following composition:

TABLE 1

	C	O	Na	P	Cl	Fe	Ni	Cu
A1	49.5	7.3	2.0	1.6	0.3	1.2	37.1	0.6
A2	30.1	8.3	3.8	2.2	0.7	1.2	51.9	0.8

TABLE 1-continued

	C	O	Na	P	Cl	Fe	Ni	Cu
A3	62.8	16.6	1.7	1.0	0.7	1.2	15.2	0.3
A4	42.3	11.4	3.3	1.6	0.9	1.3	38.0	0.5
A5	36.4	12.1	3.5	2.4	0.9	0.8	42.2	0.8
A5	56.0	8.1	2.0	1.0	0.2	0.6	30.5	0.8

Example 4

[0089] In this example, a coating comprising bismuth and tellurium was applied to a porous polymeric substrate. The substrate was a cellulose acetate (CA) membrane with a pore size of either 0.45 μm or 0.2 μm . The substrate was pre-treated by immersing in a solution containing 1 mM PdCl_2 at a pH of 5.50 for 10 to 15 minutes. The substrate was then contacted with an electroless nickel solution (a proprietary solution from Caswell) at a temperature of from 50 to 90° C. for 30 seconds. The substrate was subsequently contacted with a solution containing bismuth (III) chloride dissolved in 0.4 L 6wt % HCl, 5.2 g/L EDTA, 8.4 g/L Sodium hydroxide and Te-9.6 g/L Telluride powder, 6 g/L Sodium borohydride for a period of 3.5 hours. An outer coating comprising bismuth and telluride was formed. FIG. 5 shows an SEM photomicrograph of the coated porous material.

Examples 5 to 11

[0090] Examples 5 to 11 are set out in the table below. In examples 5 to 11, electroless deposition was used to form the final metal coatings on the porous polymeric substrate. A seed layer containing palladium chloride and tin chloride was first applied, followed by an optional accelerator step, followed by electroless deposition. Electrical conductivity of the porous material was determined. For some of the examples, the equivalent solid conductivity was also determined.

Example	Process	Parameters	Compositions used in process	Metal coatings	Substrate	Conductivity (S/cm)	Equivalent solid conductivity (S/cm)
5	Electroless	Activator—27.5° C., 3 min Accelerator—48.5° C., 1 min Cu—46.5° C., 20 mins	Sample pre-treatment: Activator—Macuplex D34C with HCl 12M Accelerator—Macuplex 9338 with 12M HCl Copper coating: MacDermid Copper 85	Copper	Fibrous, non-woven, 20 μm thickness	4506	91108
6	Electroless	Activator—27.5° C., 3 min Accelerator—48.5° C., 1 min Cu—46.5° C., 60 mins	Sample pre-treatment: Activator—Macuplex D34C with HCl 12M Accelerator—Macuplex 9338 with 12M HCl Copper coating: MacDermid Copper 85	Copper	Fibrous, non-woven, 20 μm thickness	18149	196547
7	Electroless	Activator—27.5° C., 3 min Accelerator—48.5° C., 1 min Cu—46.5° C., 120 mins	Sample pre-treatment: Activator—Macuplex D34C with HCl 12M Accelerator—Macuplex 9338 with 12M HCl Copper coating: MacDermid Copper 85	Copper	Fibrous, non-woven, 20 μm thickness	33832	280986

-continued

Example	Process	Parameters	Compositions used in process	Metal coatings	Substrate	Conductivity (S/cm)	Equivalent solid conductivity (S/cm)
8	Electroless	Activator—27.5° C., 3 min—Ni—70-75° C., 40 mins, pH 9	Sample pre-treatment: Activator—Nickel coating: 20 g/L Nickel (II) chloride, 10 g/L Sodium citrate, 35 g/L Ammonium chloride, 0.1M Sodium hypophosphite	Nickel	Fibrous, non-woven, 80 μ m thickness	6497	98572
9	Electroless	Activator—27.5 C., 3 min, Ni—60° C., 30 mins, pH 8	Sample pre-treatment: Activator—0.4 g/L PdCl ₂ with 12M HCL, 10 g/L SnCl ₂ with 12M HCL Nickel-cobalt coating: 38 g/L Nickel (II) chloride hexahydrate, 20 g/L Sodium citrate, 7.5 g/L Ammonium chloride, 0.9 g/L Cobalt (II) chloride, 2L DI H ₂ O	Nickel-Cobalt alloy/co-deposit	Fibrous, non-woven, 186 μ m thickness	1379	Not determined
10	Electroless	Activator—27.5 C., 3 min, Ni—75° C., 20 mins, pH 8	Sample pre-treatment: Activator—0.4 g/L PdCl ₂ with 12M HCL, 10 g/L SnCl ₂ with 12M HCL Nickel-cobalt coating: 38 g/L Nickel (II) chloride hexahydrate, 20 g/L Sodium citrate, 7.5 g/L Ammonium chloride, 0.9 g/L Cobalt (II) chloride, 2L DI H ₂ O	Nickel-Cobalt alloy/co-deposit	Fibrous, non-woven, 55 μ m thickness	1976	Not determined
11	Electroless	Activator—27.5 C., 3 min Accelerator—48.5 C., 1 min Cu—30-40° C., 120 mins Sn—29-30° C., 27 mins	Sample pre-treatment: Activator—Macuplex D34C with HCl 12M Accelerator—Macuplex 9338 with 12M HCl Copper coating: MacDermid Copper 85 Tin coating: Sulfuric acid, 38.05 g/L Thiourea, 21.48 g/L Tin (II) sulfate, 53 g/L Sodium hypophosphite	Copper, followed by tin	Fibrous, non-woven, 65 μ m thickness	9429	Not determined

Example 12

[0091] Substrate preparation: Cellulose acetate (CA) membranes with a pores size of 0.45 μ m and a thickness of 127 μ m and Polyethersulfone (PES) membranes with a pore size of 0.45 μ m and a thickness of 100 μ m were pre-treated to accept electroless deposition (such as by using the pre-treatment steps of examples 1 to 5), then coated using electroless deposition with either nickel or nickel followed by copper. Ni-28.3 g/L Nickel (II) sulfate, 42.03 g/L citric acid, 25 g/L sodium hydroxide, 3.3 g/L DMAB, Cu-15 g/L Copper (II) sulfate pentahydrate, 27 g/L EDTA, 8.75 g/L Sodium hydroxide, Formaldehyde—Zn Enthone CLZ-970 electrolytic plating solution. The electroless deposition was over a period of 10 minutes for nickel and three minutes for copper. The electrodeposition of zinc took place over a period of 40 minutes at 27° C. using a current of 100 mA. Metal coatings comprising nickel, copper and zinc were formed. FIGS. 6 to 8 are SEM photomicrographs showing the porous material produced in this example. Table 2 shows the composition of the coated material.

TABLE 2

	C	O	S	Ni	Cu	Zn
A2	61.0	6.1	0.6	15.0	3.5	13.4
A3	36.1	6.9	1.6	16.9	14.3	24.2
A4	42.9	11.8	2.3	15.8	10.5	16.7
A5	60.2	14.2	2.7	6.5	5.6	10.8
A6	51.6	12.1	2.2	8.0	7.0	19.2

Example 13

[0092] In this example a polymeric membrane with a non-woven fibrous composite structure and a thickness of 115 μ m was coated with nickel and iron using electroless deposition. The porous polymeric substrate was pre-treated to accept electroless deposition (such as by using the pre-treatment steps of examples 1 to 5). An electroless deposition solution comprising 0.08M Iron (II) sulfate heptahydrate, 28.3 g/L nickel (II) sulfate, 42.03 g/L citric acid, 25

g/L sodium hydroxide, 3.3 g/L DMAB was contacted with the substrate at 45° C. for a period of 12 minutes at pH 9. SEM photomicrographs are shown in FIGS. 9 and 10.

Example 14

[0093] A porous polymeric membrane such as a cellulose acetate (CA) membrane with a pore size of 0.45 μm and a thickness of 127 μm was coated using electroless deposition to form an outer coating containing gold. A combination of sensitization and activation steps was used to prepare the porous polymeric membrane for the electroless deposition of a layer of gold. The following conditions were used:

[0094] Pd—The membrane was immersed in an aqueous solution containing 1 mM PdCl₂ at pH of 5 (pH was adjusted with NaOH). The membrane was soaked in the solution for 4h. Sn—The membrane was immersed in a solution that contained 0.026M tin (II) chloride, 0.07M trifluoroacetic acid, 50%/50% methanol/water at room temperature for three minutes. Ag—The membrane was then transferred and immersed into an aqueous solution of ammoniacal silver nitrate (0.029M) at room temperature for two minutes. Au—1 ml/40 ml Oromerse part B, 0.127M sodium thiosulfate, 0.625M formaldehyde at room temperature, overnight. FIGS. 11, 12 and 13 show SEM photomicrographs of the porous material formed in this example. The composition of the various layers shown in FIG. 11 are set out in the table below (percentages given in atomic %). The gold coating extends throughout substantially all of the material. The coated material had the following composition:

TABLE 3

	C	O	Pd	Ag	Sr	Au
A1	49.7	11.4	—	0	0.8	38.1
A2	34.6	1.5	0.8	1.26	—	61.9
A3	37.7	3.1	0.8	—	—	57.7
A4	44.2	3.5	0.1	0.62	0.6	51.1
A5	46.3	11.4	0.4	0.53	0.2	41.4

Example 15

[0095] A porous Polyethersulfone (PES) substrate with a pore size of 0.45 μm was pre-treated to accept electroless deposition (such as by using the pre-treatment steps of examples 1 to 5). A layer of nickel was then deposited using electroless deposition. Sulphur was then deposited on the nickel using vapor phase deposition. The following conditions were used:

[0096] Ni—28.29 g/L nickel (II) sulfate, 42.03 g/L citric acid, 25 g/L sodium hydroxide, 3.6 g/L DMAB, at 45° C. for 60 minutes, pH 9. S—powder was placed in vapor deposition chamber under argon and not in contact with the nickel coated membrane. A temperature of 175° C. and a time of 180 minutes was used for the vapor phase deposition of sulfur. FIGS. 14 to 16 show SEM photomicrographs of the porous material obtained in this example. The composition of the regions marked in FIG. 20 are set out below (percentages given in atomic %):

TABLE 4

	C	O	Si	S	Ni	Cu	Zn
A1	25.3	27.2	0.0	12.5	33.2	1.4	0.5
A2	34.4	27.8	0.1	14.2	23.6	—	—
A3	39.8	39.2	0.1	8.4	12.4	—	0.2
A4	32.6	29.5	0.2	15.2	26.0	0.6	0.0
A5	45.1	22.0	0.5	16.2	15.8	0.5	—

Example 16

[0097] A porous polymeric membrane with a non-woven fibrous composite structure and a thickness of 115 μm was coated with copper and tin using electroless deposition. The substrate was pre-treated to accept electroless deposition (such as by using the pre-treatment steps of examples 1 to 5). The following conditions were used in the coating step:

[0098] Cu—15 g/L copper (II) sulfate pentahydrate, 27 g/L EDTA, 8.75 g/L sodium hydroxide, formaldehyde, for a period of 15 minutes. Sn—Sulfuric acid, 38.05 g/L thiourea, 21.48 g/L tin (II) sulfate, 53 g/L sodium hypophosphite, for a period of 10 minutes. FIGS. 17 to 19 show SEM photomicrographs of the porous material obtained in this example. The material had the following composition:

TABLE 5

	C	O	Sn	Cu	Sn/Cu
A1	59.7	2.1	21.8	16.2	1.3
A2	69.1	3.7	14.1	13.0	1.1
A3	64.1	2.1	14.3	19.3	0.7
A4	69.4	3.1	15.1	12.3	1.2
A5	65.2	7.9	19.0	7.7	2.5

Example 17

[0099] In this example, the porous polymeric membrane with a non-woven fibrous composite structure and a thickness of 115 μm was coated with nickel using electroless deposition followed by coating with iron and zinc using electrodeposition. The conditions used in the coating steps were as follows:

[0100] The substrate was pre-treated to accept electroless deposition (such as by using the pre-treatment steps of examples 1 to 5). Electroless coating of nickel and electroless coating of FeZn were completed under the following conditions:

[0101] Ni—28.29 g/L nickel (II) sulfate, 42.03 g/L citric acid, 25 g/L sodium hydroxide, 0.12M sodium hypophosphite, for a period of 15 minutes at 65° C. and pH 8. FeZn—0.05M Ferrous glucanate dihydrate, 0.15M zinc oxide, 6.6M potassium hydroxide at room temperature and the current of 0.96 A.

Example 18

[0102] In this example, a porous polymeric cellulose acetate (CA) substrate with a pore size of 0.45 μm and a thickness of 127 μm was coated with a coating of copper and then a coating of tin using electrodeposition. The substrate was pre-treated to accept electroless deposition (such as by using the pre-treatment steps of examples 1 to 5). Electrode-

position was then used to sequentially apply copper and then tin. The following conditions were used in the electroless and electrodeposition steps:

[0103] Cu—15 g/L Copper (II) sulfate pentahydrate, 27 g/L EDTA, 8.75 g/L sodium hydroxide, formaldehyde, 30° C., 4.5 minutes, 30mA current. Sn—15 g/L Tin methane-sulphonate, 100 g/L gluconic acid sodium salt, 0.8 g/L triton X, 0.1 g/L 2 bipyridyl, room temperature, 104 minutes, 30mA current. FIGS. 20 and 21 show SEM photomicrographs of the porous material must obtained. The composition of the layers shown in FIG. 20 is as follows (percentages given in atomic %):

TABLE 6

	C	O	Al	Cu	Sn
A1	27.7	12.8	0.4	49.0	10.2
A2	37.5	15.9	—	44.7	1.8
A3	52.4	26.4	—	20.4	0.8
A4	48.2	22.2	—	27.6	1.0
A5	36.4	16.6	—	44.7	2.4

Example 19

[0104] A porous polymeric cellulose acetate (CA) substrate with a pore size of 0.45 μm and a thickness of 127 μm was used in this example. The substrate was pre-treated to accept electroless deposition (such as by using the pre-treatment steps of examples 1 to 5). A thin nickel coating layer was applied using electroless deposition prior to the electrodeposition step. The electrodeposition step used a solution containing Ni—250 g/L Nickel (II) sulfate hexahydrate, 50 g/L nickel (II) chloride, 35 g/L boric acid. The temperature during electrodeposition was 45 to 47° C. Electrodeposition occurred over a period of 120 minutes using a current of 50 mA. A substantially uniform coating of nickel was obtained.

Example 20

[0105] In this example, an electroless copper coating was applied to a porous polymeric, non-woven substrate consisting out of polyethylene terephthalate fibers (PET). The thickness of the substrate was 15 μm . The substrate was pretreated with an activator comprising Macuplex D34C with 12M HCl. Macuplex D34C is a proprietary commercially available activator that contains palladium chloride and tin chloride. The activation step took place at 27.5° C. for a period of three minutes. The substrate was then contacted with an accelerator comprising Macuplex 9338 with 12M HCl. Contact between the accelerator and the substrate took place at 48.5° C. for a period of one minute. A copper layer was then applied by contacting the substrate with MacDermid Copper 85 at a temperature of 46.5° C. for a period of 120 minutes. FIG. 22 shows an SEM photomicrograph of the coated porous material. The coating was evenly applied. Significant porosity was retained.

Example 21

[0106] A porous polymeric membrane with a non-woven fibrous composite structure and which has a thickness of 115 μm was coated with copper and a tin-nickel alloy using electroless deposition. The following conditions were used in the coating step:

[0107] Cu—15 g/L Copper (II) sulfate pentahydrate, 27 g/L EDTA, 8.75 g/L sodium hydroxide, formaldehyde, for a period of 15 minutes. SnNi—Tin(II) chloride dehydrate 20 g/L, nickel(II) chloride hexahydrate 20 g/L, sodium hypophosphite 60 g/L, thiourea 60 g/L, citric acid monohydrate 20 g/L, tartaric acid dehydrate 40 g/L, hydrochloric acid 70 g/L for a period of 20 min at temperature between 60-75° C. The material had the following composition (percentages given in atomic %):

TABLE 7

	C	O	Sn	Ni	Cu	Sn/Ni	Ni/Cu
A1	60.8	5.4	9.4	7.1	16.8	1.3	0.4
A2	59.4	10.5	10.6	7.2	11.6	1.5	0.6
A3	66.4	8.8	8.5	6.4	9.6	1.3	0.7
A4	76.0	12.1	4.4	3.5	3.8	1.3	0.9
A5	71.5	10.9	7.1	5.1	5.3	1.4	1.0

Example 22

[0108] A porous polymeric membrane with a composite structure comprising a polyethylene and ethyl vinyl alcohol, which has a pore size of 1.5 μm and a thickness of 60 μm was coated with copper using electroless deposition. The following conditions were used in the coating step:

[0109] Cu—15 g/L Copper (II) sulfate pentahydrate, 27 g/L EDTA, 8.75 g/L sodium hydroxide, formaldehyde, for a period of 19 minutes at 30° C. FIGS. 23 and 24 show SEM photomicrographs of the porous material obtained in this example. Compositional analysis at various regions of the porous material are shown in Table 8, which shows that the copper extends throughout the thickness of the material.

TABLE 8

	C	O	Cu
A1	33.0	0.8	65.5
A2	60.2	1.1	38.3
A3	58.5	1.3	39.5
A4	65.6	1.5	32.3
A5	54.6	2.2	42.6

Example 23

[0110] A porous polymeric nylon substrate, was coated with copper using electroless deposition. The following conditions were used in the coating step:

[0111] Cu—15 g/L Copper (II) sulfate pentahydrate, 27 g/L EDTA, 8.75 g/L sodium hydroxide, formaldehyde, for a period of 30 minutes at 30° C. The substrate could be pre-treated to accept electroless deposition (such as by using the pre-treatment steps of examples 1 to 5).

Example 24

[0112] In this example, the porous polymeric membrane was a non-woven fibrous composite structure and a thickness of 115 μm . The substrate was first coated with a conductive layer by using electroless deposition to apply a layer of nickel. Electro-precipitation was then used to sequentially apply a nickel-cobalt-zinc alloy. The following conditions were used in the deposition steps:

[0113] Ni—A commercial nickel chemistry from Technic was used for the electroless deposition of the first nickel layer. The deposition was carried out for 45 minutes at 50° C.

[0114] NiCoZn—1.5M Nickel nitrate hexahydrate, 0.14M cobalt (II) chloride hexahydrate, 0.07M zinc (II) nitrate hexahydrate, room temperature, 5 h, 100 mA current.

1. A porous material comprising a porous polymeric membrane substrate having a pore size in a range from 0.1 μm to 10 μm and coated with a thin and uniform coating of one or more metals or metal alloys, the coating having a thickness that falls in the range from ~ 10 nm to ~ 1 μm , wherein the coating extends all through the thickness of the porous material and wherein the coating imparts high conductivity to the membrane such that the porous material has an equivalent conductivity of from 0.05 S/cm to 440,000 S/cm and wherein the porous material has a volume fraction of solid of less than 80%.

2. A porous material comprising a porous polymeric membrane substrate having a pore size in a range from 0.1 μm to 10 μm and coated with a thin, uniform coating of one or more metals or metal alloys, the coating having a thickness that falls in the range from ~ 10 nm to ~ 1 μm , wherein the coating extends all through the thickness of the porous material and wherein the coating imparts high conductivity to the membrane such that the porous material has an equivalent conductivity of from 10 to 440,000 S/cm and wherein the porous material has a volume fraction of coating of less than 80%.

3. A porous material as claimed in claim 1 wherein an equivalent conductivity of the porous material is at least $\sim 0.016\%$ of that obtained for thin films of similar composition and thickness deposited on solid substrates.

4. A porous material as claimed in claim 1 wherein an equivalent conductivity of the porous material is 0.0065% or greater than that obtained for solid materials of similar composition, or $\sim 1/50^{\text{th}}$ or greater than that obtained for solid materials of similar composition, or $\sim 1/20^{\text{th}}$ or greater than that obtained for solid materials of similar composition, or $\sim 1/10^{\text{th}}$ or greater than that obtained for solid materials of similar composition, or $\sim 1/5^{\text{th}}$ or greater than that obtained for solid materials of similar composition, or $1/2$ or greater than that obtained for solid materials of similar composition.

5. A porous material as claimed in claim 1 wherein an equivalent solid conductivity of the porous material ranges from about 10 S/cm to 281000 S/cm, or from 10 S/cm to 1500 S/cm, or 100 S/cm to 1500 S/cm.

6. A porous material as claimed in claim 1 wherein the one or more metals or metal alloys is selected from the group consisting of copper, tin, nickel, iron, aluminum, titanium, cobalt, zinc, manganese, silver, gold, antimony, cadmium, tellurium, bismuth, platinum, palladium, ruthenium, rhodium, chromium, magnesium, calcium, beryllium, zirconium, molybdenum, lead, vanadium, potassium, niobium, cadmium, iridium, osmium, rhenium, indium, gallium, germanium, thallium, selenium and alloys thereof, and alloys comprising SnNi, SnFe, SnBi, SnSe, SnSb, SnSbNi, SnSbCo, CuSn, CuZn, Mg_2Si , MnSn, MgSn, alloys based on the combination of titanium and aluminum.

7. A porous material as claimed in claim 1 wherein the material is post-treated to add additional functionality.

8. A porous material as claimed in claim 1 wherein the different material of the coating comprises nanoparticles such that the nanoparticles are applied to a surface of the substrate.

9. A porous material as claimed in claim 1 wherein the coating comprises nanolayers of the different material.

10. A porous material as claimed in claim 9 wherein the coating comprises a plurality of nanolayers.

11. A porous material as claimed in claim 1 wherein the porous material has a ratio of compressive strength (measured in Mpa) to volume fraction of solids (measured as volume fraction) of greater than 5 Mpa/ v_f or greater than 10 Mpa/ v_f or greater than 50 Mpa/ v_f or greater than 100 Mpa/ v_f .

12. A porous material as claimed in claim 1 wherein a thin layer of solid material is placed on top of the uniform coating, to provide a contacting surface.

13. A porous material comprising a porous polymeric membrane substrate having a pore size in a range from 0.1 μm to 10 μm and coated with a thin, uniform coating of a one or more metals or metal alloys wherein the coating extends all through the thickness of the porous material and wherein the coating imparts high conductivity to the membrane and wherein the porous material has a volume fraction of solid of less than 50%, or less than 40%, or less than 30%, or less than 25% or less than 5.5% wherein the porous material has a ratio of compressive strength (measured in Mpa) to volume fraction of solids (measured as volume fraction) of greater than 5 Mpa/ v_f or greater than 10 Mpa/ v_f or greater than 50 Mpa/ v_f or greater than 100 Mpa/ v_f .

14. A porous material comprising a porous polymeric membrane substrate having a pore size in a range from 0.1 μm to 10 μm and coated with a thin, uniform coating of one or more metals or metal alloys wherein the coating extends all through the thickness of the porous material and wherein the coating imparts an equivalent solid conductivity in the range of 0.05 S/cm to 440,000 S/cm to the membrane and wherein the porous material has a volume fraction of solid of less than 50%, or less than 40%, or less than 30%, or less than 25% or less than 5.5%.

15. A porous material comprising a porous polymeric membrane substrate having a pore size in a range from 0.1 μm to 10 μm and coated with a thin, uniform coating of one or more metals or metal alloys wherein the coating extends all through the thickness of the porous material and wherein the coating imparts an equivalent solid conductivity in the range of 0.05 S/cm to 1500 S/cm to the membrane and wherein the porous material has a volume fraction of coating of less than 50%, or less than 40%, or less than 30%, or less than 25% or less than 5.5%.

16. A porous material comprising a porous polymeric membrane substrate having a pore size in a range from 0.1 μm to 10 μm and coated with a thin uniform coating of one or more metals or metal alloys, the coating having a thickness that falls within the range of from ~ 10 nm to ~ 200 nm wherein the coating extends all through the thickness of the porous material and wherein the coating imparts an equivalent solid conductivity in the range of 0.05 S/cm to 1500 S/cm to the membrane and wherein the porous material has a volume fraction of solid of less than 50%, or less than 40%, or less than 30%, or less than 25% or less than 5.5%.

17. A porous material comprising a porous polymeric membrane substrate having a pore size in a range from 0.1 μm to 10 μm and coated with a thin uniform coating of a

different material, the coating having a thickness that falls within the range of from ~10 nm to ~200 nm wherein the coating extends all through the thickness of the porous material and wherein the coating imparts an equivalent solid conductivity in the range of 0.05 S/cm to 1500 S/cm to the membrane and wherein the porous material has a volume fraction of coating of less than 50%, or less than 40%, or less than 30%, or less than 25% or less than 5.5%.

18. A porous material as claimed in claim 1 wherein the coating has a thickness that falls in the range of from ~10 nm to ~860 nm, or from ~10 nm to ~300 nm, or from ~10 nm to ~280 nm, or from ~10 nm to ~260 nm, or from ~10 nm to ~200 nm.

19. A porous material as claimed in claim 1 wherein the coating further comprises sulfur.

20. A porous material as claimed in claim 19 wherein the sulfur is present as a distinct layer.

21. A porous material as claimed in claim 19 wherein the sulfur is intimately mixed with one or more of the metals or metal alloys.

22. A porous material as claimed in claim 1 wherein the one or more metal alloys contain cobalt and one or more other metals.

23. A porous material as claimed in claim 1 wherein the volume fraction of solid is less than 50%, or less than 40%, or less than 30%, or less than 25% or less than 5.5%.

24. A porous material as claimed in claim 2 wherein the volume fraction of solid is less than 50%, or less than 40%, or less than 30%, or less than 25% or less than 5.5%.

25. A porous material as claimed in claim 6 wherein the one or more metals or metal alloys are selected from copper, tin, nickel, iron, aluminium, titanium, cobalt, zinc, manganese, silver, gold, and alloys thereof.

26. A porous material comprising a porous polymeric membrane substrate having a pore size in a range from 0.1 μm to 10 μm and coated with a thin and uniform coating of one or more metal phosphides, the coating having a thickness that falls in the range from ~10 nm to ~1 μm , wherein the coating extends all through the thickness of the porous material and wherein the coating imparts high conductivity to the membrane such that the porous material has an equivalent conductivity of from 0.05 S/cm to 440,000 S/cm and wherein the porous material has a volume fraction of solid of less than 80%.

27. A porous material as claimed in claim 26 wherein the one or more metal phosphides are selected from one or more of copper phosphide, iron phosphide, tin phosphide, and nickel phosphide.

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