

(12) **United States Patent**
Mansky et al.(10) **Patent No.:** **US 6,668,230 B2**
(45) **Date of Patent:** **Dec. 23, 2003**(54) **COMPUTER READABLE MEDIUM FOR
PERFORMING SENSOR ARRAY BASED
MATERIALS CHARACTERIZATION**(75) Inventors: **Paul Mansky**, San Francisco, CA (US);
James Bennett, Santa Clara, CA (US)(73) Assignee: **Symyx Technologies, Inc.**, Santa Clara,
CA (US)(*) Notice: Subject to any disclaimer, the term of this
patent is extended or adjusted under 35
U.S.C. 154(b) by 0 days.(21) Appl. No.: **10/315,519**(22) Filed: **Dec. 10, 2002**(65) **Prior Publication Data**

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10, 1999, now Pat. No. 6,535,824, which is a continuation-
in-part of application No. 09/210,086, filed on Dec. 11,
1998, now Pat. No. 6,438,497, and a continuation-in-part of
application No. 09/210,428, filed on Dec. 11, 1998, now Pat.
No. 6,477,479, and a continuation-in-part of application No.
09/210,485, filed on Dec. 11, 1998.(51) **Int. Cl.**⁷ **G01N 31/00**(52) **U.S. Cl.** **702/30; 702/22; 702/104;**
702/130; 422/68.1; 422/98; 422/82.01;
73/863.01; 73/863.21; 700/266; 700/268;
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130, 132, 136, 183, 189; 422/82.12, 99,
108, 82.02; 374/49, 50, 56; 73/863, 863.01,
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406-410; 700/266, 268, 269, 299, 300;
435/DIG. 1, DIG. 22; 436/43, 55, 148,
149; 205/335, 770(56) **References Cited****U.S. PATENT DOCUMENTS**

3,266,307 A 8/1966 DeWinter 73/190

(List continued on next page.)

FOREIGN PATENT DOCUMENTS

DE 198 05 719 12/1998

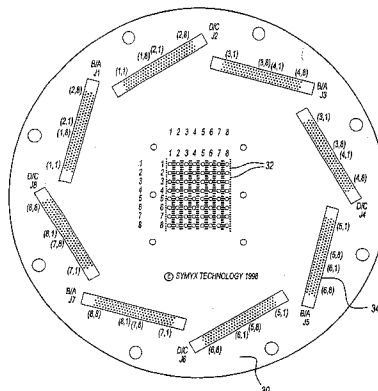
(List continued on next page.)

OTHER PUBLICATIONSHasanuzzaman et al., Process Compilation of Thing Film
Microdevices 1996, IEEE, vol:0070, pp. 745-764.*

(List continued on next page.)

Primary Examiner—Marc S. Hoff*Assistant Examiner*—Elias Desta(74) *Attorney, Agent, or Firm*—Dobrusin & Thennisch PC(57) **ABSTRACT**

A modular materials characterization apparatus includes a sensor array disposed on a substrate, with a standardized array and contact pad format; electronic test and measurement apparatus for sending electrical signals to and receiving electrical signals from the sensor array; an apparatus for making electrical contact to the sensors in the standardized array format; an apparatus for routing signals between one or more selected sensors and the electronic test and measurement apparatus and a computer including a computer readable having a computer program recorded therein for controlling the operator of the apparatus. The sensor array is preferably arranged in a standardized format used in combinatorial chemistry applications for rapid deposition of sample materials on the sensor array. The interconnection apparatus and sensor array and contact pad allow measurement of many different material properties by using substrates carrying different sensor types, with only minor modifications if any to the electronic test and measurement apparatus and test procedures. By using a sensor array that is separate from the electronic apparatus, and by including standardized contacting and signal routing apparatuses, the apparatus creates a modular "plug-and-play" system that eliminates the need for multiple materials characterization machines, and eliminates the need for application-specific active circuitry within the sensor arrays themselves. Further, the modular sensor array system can characterize large numbers of material samples rapidly, on the order of at least 50 samples per hour, reducing the time needed for screening of materials libraries.

39 Claims, 32 Drawing Sheets

U.S. PATENT DOCUMENTS

3,789,662 A 2/1974 Zettler et al. 73/190
 4,350,446 A 9/1982 Johnson 374/13
 4,423,371 A 12/1983 Senturia et al.
 4,448,943 A 5/1984 Golba, Jr. et al.
 4,571,543 A 2/1986 Raymond et al.
 4,596,697 A 6/1986 Ballato
 4,675,674 A 6/1987 Hope
 4,710,550 A 12/1987 Kranbuehl
 4,723,908 A 2/1988 Kranbuehl
 4,743,954 A 5/1988 Brown
 4,767,719 A 8/1988 Finlan
 4,874,250 A 10/1989 Gonner 374/43
 4,891,591 A 1/1990 Johnston et al.
 4,950,608 A 8/1990 Kishimoto 435/290
 5,063,081 A 11/1991 Cozzette et al.
 5,095,278 A 3/1992 Hendrick
 5,098,196 A 3/1992 O'Neill
 5,164,319 A 11/1992 Hafeman et al.
 5,179,028 A 1/1993 Vali et al.
 5,224,775 A 7/1993 Reading et al. 374/11
 5,228,114 A 7/1993 Suzuki 392/416
 5,283,037 A 2/1994 Baer et al.
 5,296,374 A 3/1994 Culshaw et al.
 5,306,644 A 4/1994 Myerholtz et al.
 5,335,993 A 8/1994 Marcus et al. 374/11
 5,345,213 A 9/1994 Semancik et al.
 5,346,306 A 9/1994 Reading et al. 374/10
 5,356,756 A 10/1994 Cavicchi et al.
 5,439,291 A 8/1995 Reading 374/11
 5,445,008 A 8/1995 Wachter et al.
 5,464,966 A 11/1995 Gaiten et al. 219/544
 5,474,385 A 12/1995 Reading 374/11
 5,491,097 A 2/1996 Ribi et al.
 5,525,300 A 6/1996 Danssaert et al. 422/99
 5,532,128 A 7/1996 Eggers et al.
 5,533,393 A 7/1996 Bonne et al.
 5,534,111 A 7/1996 Hocker et al.
 5,557,972 A 9/1996 Jacobs et al.
 5,571,401 A 11/1996 Lewis et al.
 5,597,957 A 1/1997 Schieferdecker et al.
 5,599,104 A 2/1997 Nakamura et al. 374/12
 5,601,141 A 2/1997 Gordon et al. 165/263
 5,602,393 A 2/1997 Gerard
 5,622,633 A 4/1997 Ohtsuka et al.
 5,632,957 A 5/1997 Heller et al.
 5,634,718 A 6/1997 Martinis et al.
 5,635,845 A 6/1997 Strong et al.
 5,639,423 A 6/1997 Northrup et al.
 5,641,391 A 6/1997 Hunter et al.
 5,641,634 A 6/1997 Mandecki
 5,653,939 A 8/1997 Hollis et al. 422/50
 5,659,127 A 8/1997 Shie et al.
 5,667,667 A 9/1997 Southern
 5,668,303 A 9/1997 Giesler et al.
 5,670,322 A 9/1997 Eggers et al.
 5,698,089 A 12/1997 Lewis et al.
 5,705,399 A 1/1998 Larue
 5,739,686 A 4/1998 Naughton et al.
 5,751,629 A * 5/1998 Nova et al. 365/151
 5,755,942 A 5/1998 Zanzucchi et al. 204/454
 5,759,493 A 6/1998 Raisanen
 5,766,934 A 6/1998 Guiseppi-Elie
 5,770,038 A 6/1998 Iwama et al.
 5,776,359 A 7/1998 Schultz et al.
 5,779,362 A 7/1998 Lightfoot 374/33
 5,779,981 A 7/1998 Danssaert et al. 422/99
 5,783,805 A 7/1998 Katzmann
 5,788,373 A 8/1998 Huetter et al. 374/10
 5,788,833 A 8/1998 Lewis et al. 205/787
 6,789,168 * 8/1998 Wang et al. 436/37

5,806,979 A 9/1998 Gschneidner, Jr. et al.
 5,813,763 A 9/1998 Plotnikov et al. 374/11
 5,821,596 A 10/1998 Miu et al. 257/419
 5,832,411 A 11/1998 Schatzmann et al.
 5,876,118 A 3/1999 Vogel 374/11
 5,891,395 A 4/1999 Glaunsinger et al.
 5,923,421 A 7/1999 Rajic et al. 356/328
 5,939,312 A 8/1999 Baier et al. 435/287.2
 5,945,069 A 8/1999 Buehler
 6,017,144 A 1/2000 Guo et al.
 6,037,167 A 3/2000 Adelman et al.
 6,045,671 A 4/2000 Wu et al.
 6,079,873 A 6/2000 Cavicchi et al. 374/10
 6,093,302 A 7/2000 Montgomery
 6,111,520 A 8/2000 Allen et al.
 6,167,748 B1 1/2001 Britton, Jr. et al.
 6,170,318 B1 1/2001 Lewis
 6,215,898 B1 4/2001 Woodfill et al.
 6,290,911 B1 9/2001 Lewis et al.
 6,338,112 B1 1/2002 Wipfel et al.
 6,350,369 B1 2/2002 Lewis et al.
 6,387,329 B1 5/2002 Lewis et al.
 6,438,497 B1 8/2002 Mansky et al.
 6,477,479 B1 11/2002 Mansky et al.
 6,495,369 B1 * 12/2002 Kercso et al. 436/47

FOREIGN PATENT DOCUMENTS

JP	10-260147	9/1998
JP	10-325821	12/1998
WO	PCT/US98/07799	4/1998

OTHER PUBLICATIONS

Notification of Reasons for Refusal dated Jan. 21, 2003.
 Sullivan, P.F. and G. Seidel "Steady-state, AC-temperature calorimetry" *Physical Review* vol. 73 No. 3; Sep. 15, 1968: pp. 679-685.
 "Micron Scale Differential Scanning Calorimeter," <http://www.cstl.nist.gov/div836/836.04/SensorProj/Microcal.html>.
 "Sensor Platforms," <http://www.cstl.nist.gov/div836/836.04/SensorProj/SensorPlatforms.html>.
 "Thermodynamic Measurements of Magnetic Ordering in Antiferromagnetic Superlattices," E.N. Abarra, K. Takano, F. Hellman, and A.E. Berkowitz, *Physical Review Letters*, vol. 77, No. 16, Oct., 14, 1996, pp. 3451-3454.
 "The Anatomy of Microcalorimeter," Kim Allen, <http://physics.ucsd.edu/~kallen/Microcal/calorimeter.html>.
 "Heat Capacity Measurements on Small Samples at Low Temperature," R. Bachmann, F.J. DiSalvo, Jr., T.H. Geballe, R.L. Greene, R.E. Howard, C.N. King, H.C. Kirsch, K.N. Lee, R.E. Schwall, H.U. Thomas, R.B. Zubeck, *The Review of Scientific Instruments*, vol. 43, No. 2, Feb. 1972, pp. 205-214.
 "Micromechanical Thermogravimetry," R. Berger, H.P. Lang, Ch. Gerber, J.K. Gimzewski, J.H. Fabian, L. Scandella, E. Meyer, H.J. Guntherodt, *Chemical Physics Letters*, vol. 294, Sep. 18, 1998, pp. 363-369.
 "An Ultrahigh Vacuum Single Crystal Adsorption Microcalorimeter," C.E. Borroni-Bird and D.A. King, *Rev. Sci. Instrum.*, vol. 62, No. 9, Sep. 1991, pp. 2177-2185.
 "Relaxation Phenomena in Dense, Glassy, Membranes Prepared from a Polymer Solution, Monitored by Changes in Dielectric Properties," R.H.B. Bourn, Th. van den Boomgaard, C.A. Smolders, H. Strathmann, P.F. Mijnlief, *Journal of Membrane Science*, vol. 113, 1996, pp. 205-221.

- "A Class of Cobalt Oxide Magnetoresistance Materials Discovered with Combinatorial Synthesis," Gabriel Briceno, Haueyee Chang, Xiaodong Sun, Peter G. Schultz, X.D. Xiang, *Science*, vol. 270, Oct. 13, 1995, pp. 273-275.
- "Thermal Conductivity Measurement from 30 to 750 K: the 3∞ Method," David G. Cahill, *Rev. Sci. Instrum.*, vol. 61, No. 2, Feb. 1990, pp. 802-808.
- "Thermal Conductivity of a-Si:H Thin Films," David G. Cahill, M. Katiyar, and J.R. Abelson, *The American Physical Society*, vol. 50, No. 9, Sep. 1, 1994, pp. 6077-6081.
- "Pulsed Desorption Kinetics Using Micromachined Micro-hotplate Arrays," Richard E. Cavicchi, Gregory E. Poirier, John S. Suehle, Michael Gaitan, Steve Semancik, and Donald R. F. Burgess, *J. Vac. Sci. Technol.*, vol. 12, No. 4, Jul./Aug. 1994, pp. 2549-2553.
- "A Combinational Chemistry Approach to Oxidation Catalyst Discovery and Optimization," Peigun Cong, Dan Giaquinta, Shenhong Guan, Eric McFarland, Kyle Self, Howard Turner and W. Henry Weinburg, *Process Miniaturization: 2nd International Conference on Microreaction Technology Brochure*, pp. 118-123.
- "Thin Film Microcalorimeter for Heat Capacity Measurements from 1.5 to 800 K," D.W. Denlinger, E.N. Abarra, Kimberly Allen, P.W. Rooney, M.T. Messer, S.K. Watson, and F. Hellman, *Rev. Sci. Instrum.*, vol. 65, No. 4, Apr. 1994, pp. 946-958.
- "Plastification During Sorption of Polymeric Thin Films: A Quartz Resonator Study," Arno Dornack and Diethelm Johannsmann, *J. Appl. Phys.*, vol. 80, No. 5, Sep. 1, 1996, pp. 2599-2604.
- "A Silicon on Sapphire Thermometer for Small Sample Low Temperature Calorimetry," S. R. Early, F. Hellman, J. Marshall, and T. H. Geballe, *Physics*, vol. 107B, pp. 327-328.
- "Nanocalorimeter for High Resolution Measurements of Low Temperature Heat Capacities of Thin Films and Single Crystals," Fernando Forninaya, Thierry Fournier, Philippe Gandit, and Jacques Chaussy, *Rev. Sci. Instrum.*, vol. 68, No. 11, Nov. 1997, pp. 4191-4195.
- "Heat Capacity Cryostat and Novel Methods of Analysis for Small Specimens in the 1.5-10 K Range," E. M. Forgan and S. Nedjat, *Rev. Sci. Instrum.*, vol. 51, No. 4, Apr. 1980, pp. 411-417.
- "Thermal Conductivity and Diffusivity Measurements in the sub- μ s Scale on Centimeter Area Samples Using a Micro-thermocouple," R. Forster and E. Grnlin, *Rev. Sci. Instrum.*, vol. 67, No. 12, Dec. 1996, pp. 4246-4255.
- "An AC Calorimeter for Measuring Heat Capacity of Free-Standing Liquid-Crystal Films," R. Geer, T. Stoebe, T. Pitchford, and C.C. Huang, *Rev. Sci. Instrum.*, vol. 62, No. 2, Feb. 1991, pp. 415-421.
- Abstract, "Microcalorimetric Study of the Acidic Character of Modified Metal Oxide Surfaces. Influence of the Loading Amount on Alumina, Magnesia, and Silica," A. Gervasini, *Langmuir*, vol. 12, 1996, pp. 5356-5364.
- "Modulated-bath Calorimetry," J.E. Graebner, *Rev. Sci. Instrum.*, vol. 60, No. 6, Jun. 1989, pp. 1123-1128.
- "Specific Heat of Granular Aluminum Films," R.L. Greene, C.N. King, and R.B. Zubeck, *Physical Review B*, vol. 6, No. 9, Nov. 1, 1972, pp. 3297-3304.
- Abstract, "Localized Thermal Analysis Using a Mechanical Resistive Probe," A. Hammiche, M. Reading, H.M. Pollock, and M. Song, *Rev. Sci. Instrum.*, vol. 67, No. 12, Dec. 1996, pp. 4268-4274.
- "Nanocalorimeter for Explorations of Mesoscopic Heat Flow," E.A. Henriksen, K.C. Schwab, J.M. Worlock, M.L. Roukes, <http://www.cmp.caltech.edu/~lifshitz/march98/abs98.h>.
- "Experimental Limitations in Impedance Spectroscopy of Materials Systems," G. Hsieh, D.D. Edwards, S.J. Ford, J.H. Hwang, J. Shane, E.J. Garboczi, and T.O. Mason, *Mat. Res. Soc. Symp. Proc.*, vol. 411, 1996, pp. 3-13.
- "Visco-elastic Properties of Thin Films Probed with a Quartz Crystal Resonator," D. Johannsmann, F. Embs, C.G. Willson, G. Wegner, and W. Knoll, *Makromol. Chem., Macromol. Symp.*, vol. 46, 1991, pp. 247-251.
- "Dielectric Monitoring of Polymerization and Cure," David E. Kranbuehl, *Dielectric Spectroscopy of Polymeric Materials*, pp. 303-328.
- "Microcalorimeters May Provide a Solution to the Big Problem of Small Contaminants," Ray Ladbury, *Physics Today*, Jul. 1998, pp. 19-21.
- "Heat Capacity Measurements of Sn Nanostructures Using a Thin-Film Differential Scanning Calorimeter with 0.2 nJ Sensitivity," S.L. Lai, G. Ramanath, L.H. Allen, and P. Infante, *Appl. Phys. Lett.*, vol. 70, No. 1, Jan. 6, 1997, pp. 43-45.
- "High-Speed (10^4 °C/s) Scanning Microcalorimetry with Monolayer Sensitivity (J/m^2)," S.L. Lai, G. Ramanath, and L.H. Allen, *Appl. Phys. Lett.*, vol. 67, No. 9, Aug. 28, 1995, pp. 1229-1231.
- "Size-Dependent Melting Properties of Small Tin Particles: Nanocalorimetric Measurements," S.L. Lai, J.Y. Guo, V. Petrova, G. Ramanath, and L.H. Allen, *Physical Review Letters*, vol. 77, No. 1, Jul. 1, 1996, pp. 99-102.
- "Determination of Complex Shear Modulus with Thickness Shear Mode Resonators," Ralph Lucklum, Carsten Behling, Richard W. Cernosek, and Stephen J. Martin, *JOP Publishing*, Sep. 1996, pp. 346-356.
- "Materials Test Equipment -Materials Measurement Systems," 1998 Hewlett-Packard Test and Measurement Catalog, pp. 349-351.
- " μ TA 2990 Micro-Thermal Analyzer -Characterizing the Nano-World," *TA Instruments Thermal Analysis & Rheology Brochure*.
- "A 3-350 K Fast Automatic Small Sample Calorimeter," V.K. Pecharsky, J.O. Moorman, and K.A. Gschneider, Jr., *Rev. Sci. Instrum.*, vol. 68, No. 11, Nov. 1997, pp. 4196-4207.
- "The Broad Sweep of Integrated Microsystems," S. Tom Picraux and Paul J. McWhorter, *IEEE Spectrum*, Dec. 1998, pp. 24-33.
- "A Very Sensitive Microcalorimetry Technique for Measuring Specific Heat of μ g Single Crystals," O. Riou, P. Gandit, M. Charalambous, and J. Chaussy, *Rev. Sci. Instrum.*, vol. 68, No. 3, Mar. 1997, pp. 1501-1509.
- "Measurement of Low-Temperature Specific Heat," G.R. Stewart, *Rev. Sci. Instrum.*, vol. 54, No. 1, Jan. 1983, pp. 1-11.
- "A Study of Low-Cost Sensors for Measuring Low Relative Humidity," P.R. Story, D.W. Galipeau, R.D. Milcham, *Sensors and Actuators B*, vol. 24-25, 1995, pp. 681-685.
- "Microcalorimetric Study of Ethylene on Pt(110)-(1 x 2)," A. Struck, C.E. Wartnaby, Y.Y. Yeo, and D.A. King, *Physical Review Letters*, vol. 74, No. 4, Jan. 23, 1995, pp. 578-581.
- "Steady-State, ac-Temperature Calorimetry," Paul F. Sullivan and G. Seidel, *Physical Review*, vol. 173, No. 3, Sep. 15, 1968, pp. 679-685.

"AC Temperature Calorimetry for Thin Films at Low Temperatures," Takao Suzuki, Takefumi Tsuboi, and Hideo Takai, *Japanese Journal of Applied Physics*, vol. 21, No. 2, Feb. 1982, pp. 368-372.

Abstract, "An Apparatus for Measuring the Thermal Conductivity and Viscosity of Polymers Under Shearing Strain," I.H. Tavman, *Meas. Sci. Technol.*, vol. 8, 1997, pp. 287-292.

"In-Plane Permittivity of Spin-Cast Polymer Films," Shari A. Weinberg and Sue Ann Bidstrup-Allen, *Mat. Res. Soc. Symp. Proc.*, vol. 411, 1996, pp. 229-234.

"Specific Heat Measurements by Non-Contact Calorimetry" R.K. Wunderlich and H.J. Fecht, *Journal of Non-Crystalline Solids*, vol. 156-158, 1993, pp. 421-424.

"A Combinatorial Approach to Materials Discovery," X.D. Xiant, Xiadong Sun, Gabriel Briceno, YulinLou, Kai-An Wang, Hauyee Chang, William G. Wallace-Freedman, Sung-Wei Chen, and Peter G. Schultz, *Science*, vol. 268, Jun. 23, 1995, pp. 1738-1740.

"A Capacitance Sensor for On-Line Monitoring of Ultrathin Polymeric Film Growth," Guo-Gang Zhou, Stephen T.

Kowel, and M.P. Srinivasan, *IEEE Transactions on Components, Hybrids, and Manufacturing Technology*, vol. 11, No., 2, Jun. 1998, pp. 184-190.

Semancik, Steve and Richard Cavicchi, "Kinetically Controlled Chemical Sensing Using Micromachined Structures," *Accounts of Chemical Research*, vo. 31 (No. 5), pp. 279-287, (1998).

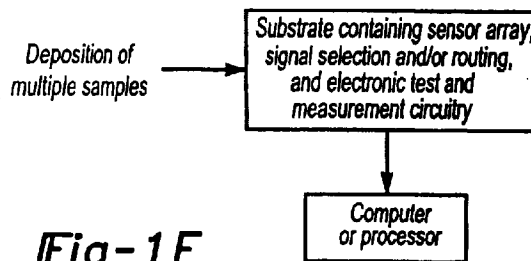
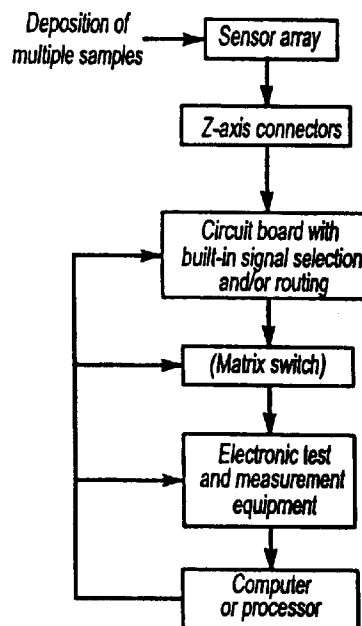
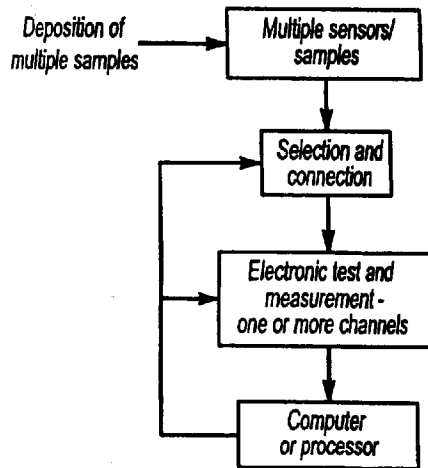
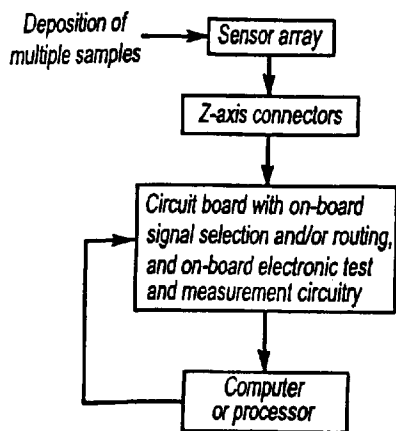
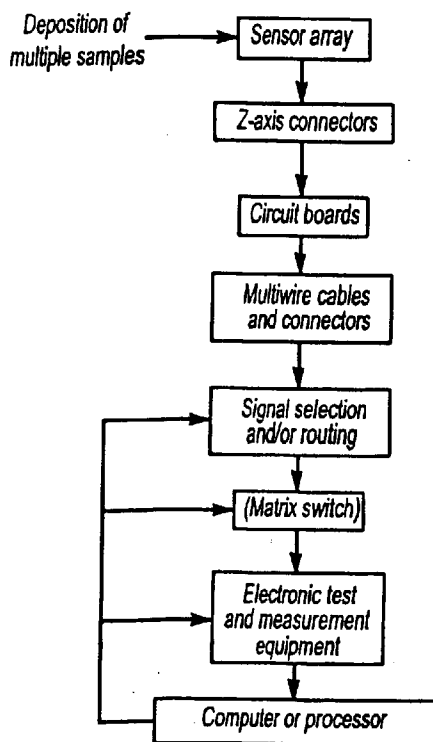
Copending Application Ser. No. 09/863,532 filed May 23, 2001.

Copending Application Ser. No. 09/858,048 filed May 15, 2001.

Protest received by Technology Center 2800 mailed May 29, 2001 in Ser. No. 09/210,485.

Applicants' Reply to Protest filed on Jun. 25, 2001 in Ser. No. 09/210,485 with attachments.

* cited by examiner



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