United States Patent

Tolk et al.

[15] **3,644,044**

[45] **Feb. 22, 1972**

[54] METHOD OF ANALYZING A SOLID SURFACE FROM PHOTON EMISSIONS OF SPUTTERED PARTICLES

[72] Inventors: **Norman Henry Tolk, Westfield; Clark Woody White, Dover, both of N.J.**

[73] Assignee: **Bell Telephone Laboratories Incorporated,** Murray Hill, N.J.

[22] Filed: **May 20, 1970**

[21] Appl. No.: **38,961**

[52] **U.S. Cl.** .....**356/85,** 250/49.5 P, 250/71 R

[51] **Int. Cl.** **H01j 37/26,** G01j 3/30

[58] **Field of Search**.....250/49.5 P, 71 R; 356/85

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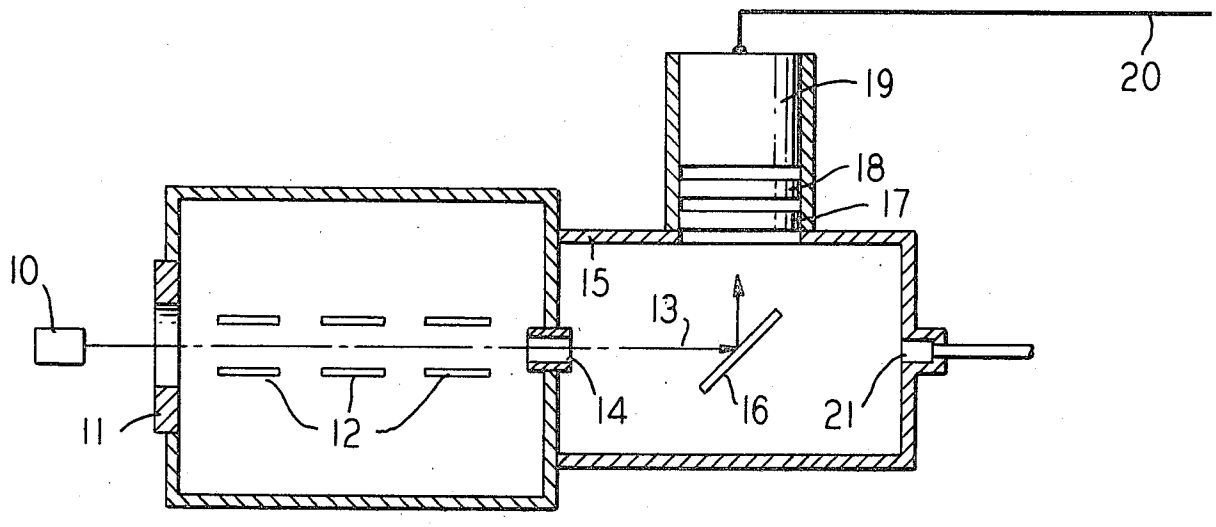
Primary Examiner—Anthony L. Birch

Attorney—R. J. Guenther and Edwin B. Cave

[57] **ABSTRACT**

Identification of unknown constituents and their relative concentrations in a solid surface is made by bombarding the solid surface with an ion or molecule beam having low energy and low density, so as to achieve the sputtering of excited particles directly from the surface and resultant photon emissions characteristic of the sputtered particles.

6 Claims, 12 Drawing Figures



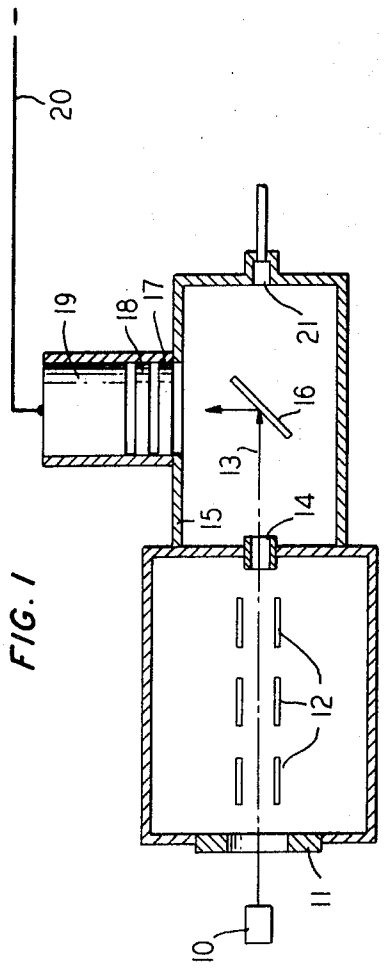


FIG. 1

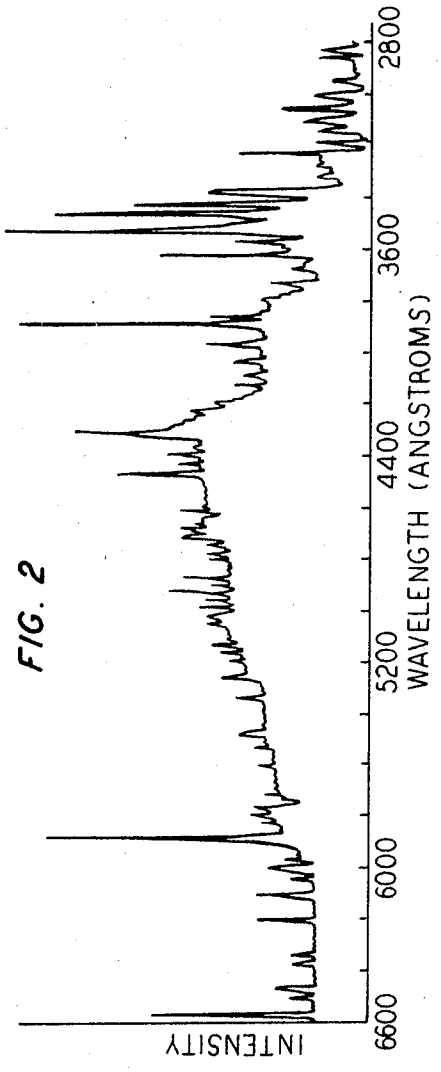


FIG. 2

INVENTORS N. H. TOLK
C. W. WHITE
BY George S. Sprague
ATTORNEY

FIG. 3

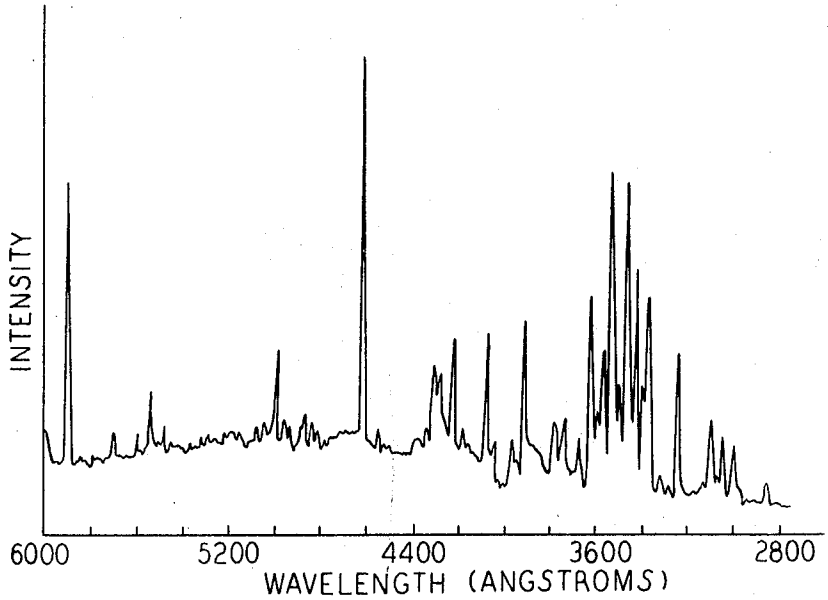

INTENSITY
6000
5200
4400
3600
2800
WAVELENGTH (ANGSTROMS)

FIG. 4

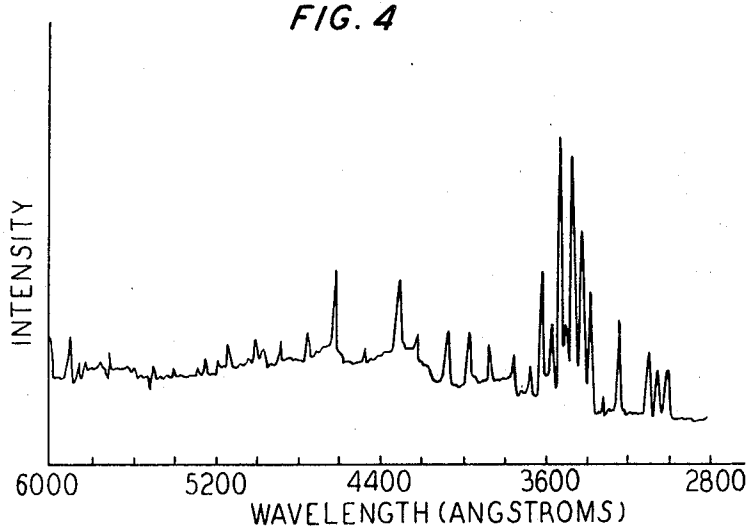

INTENSITY
6000
5200
4400
3600
2800
WAVELENGTH (ANGSTROMS)

FIG. 5

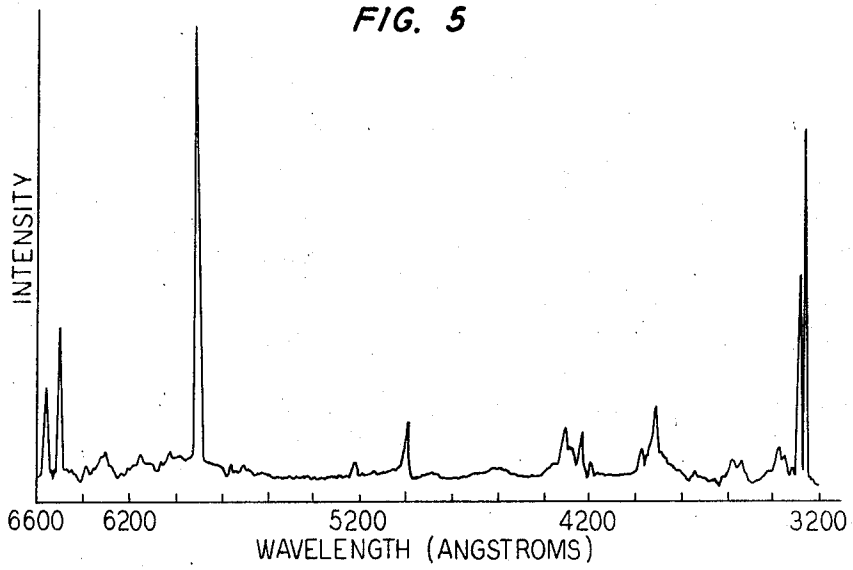


FIG. 6

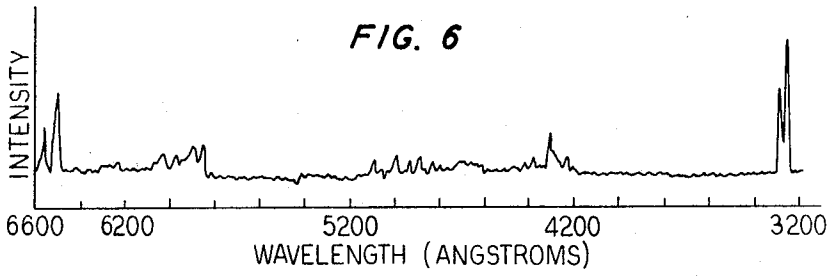


FIG. 7

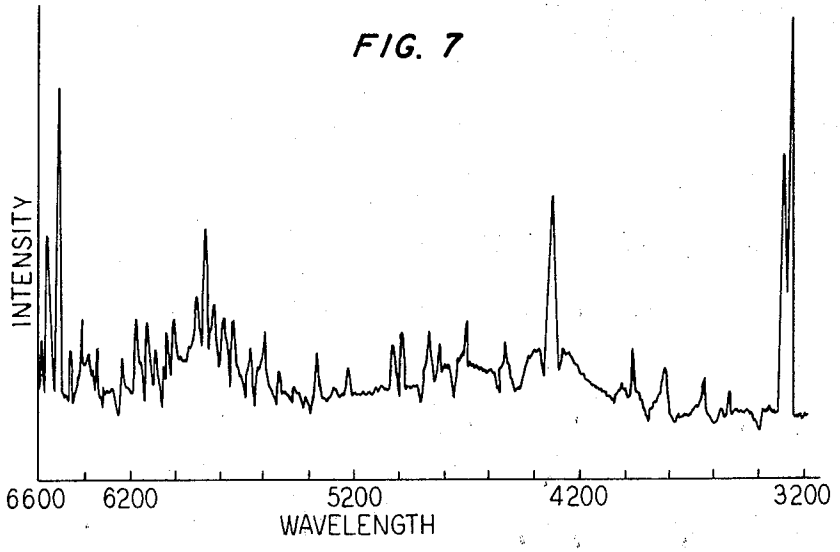


FIG. 8

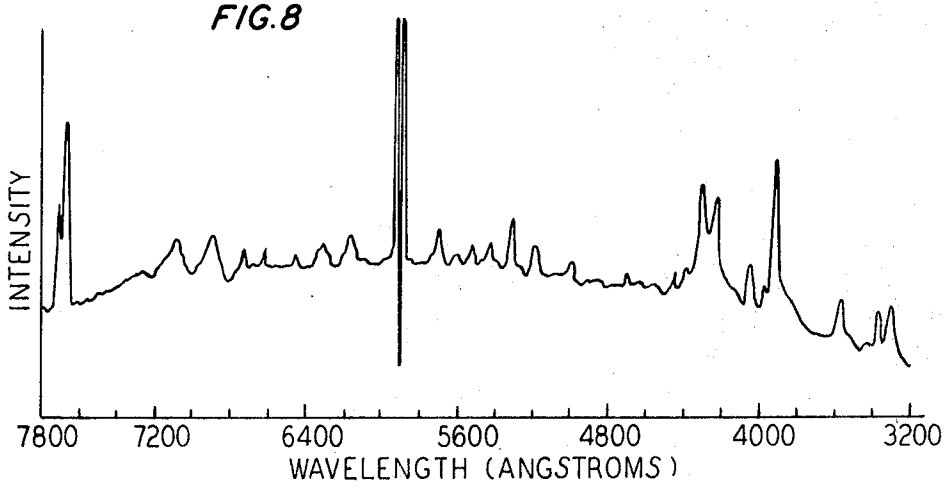


FIG. 9

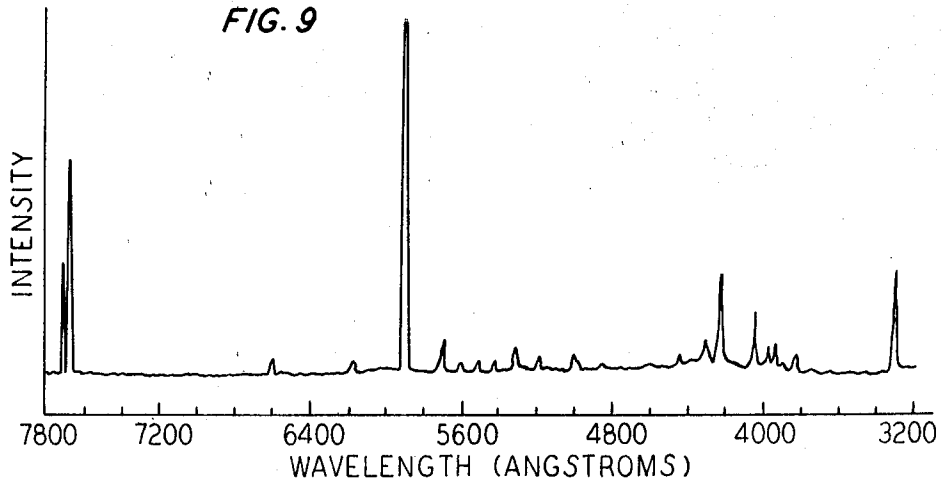


FIG. 12

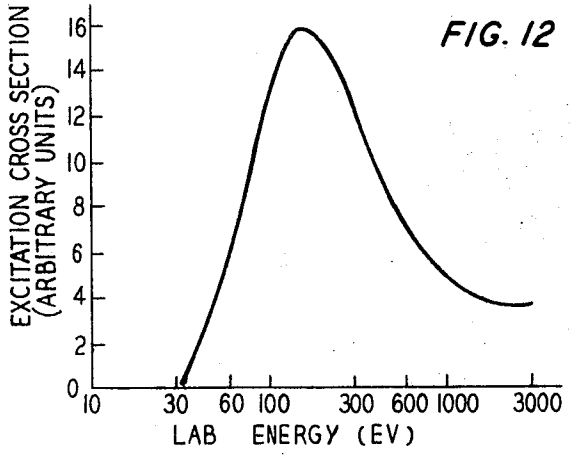


FIG. 10

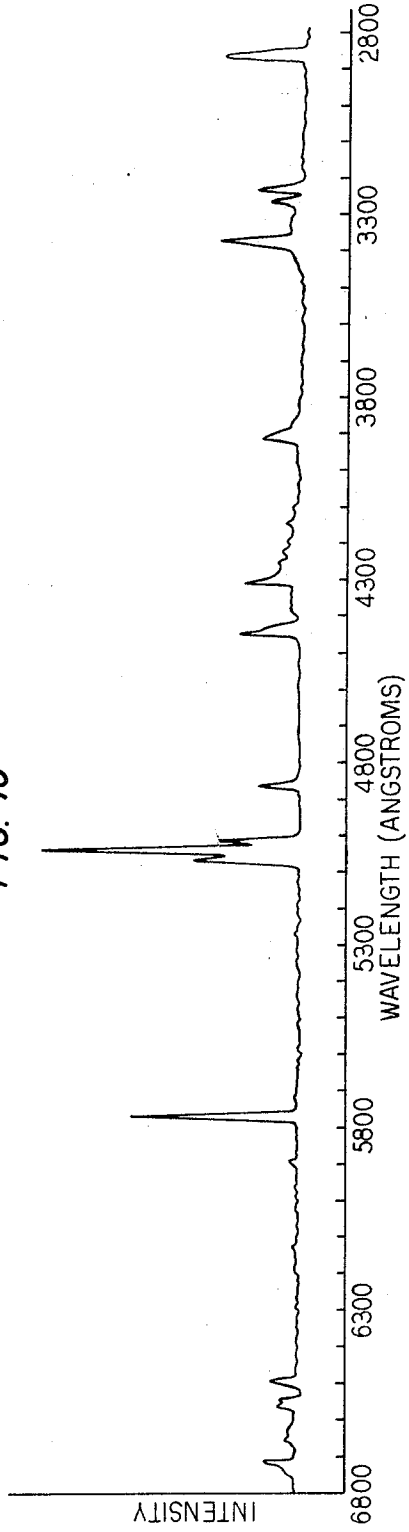
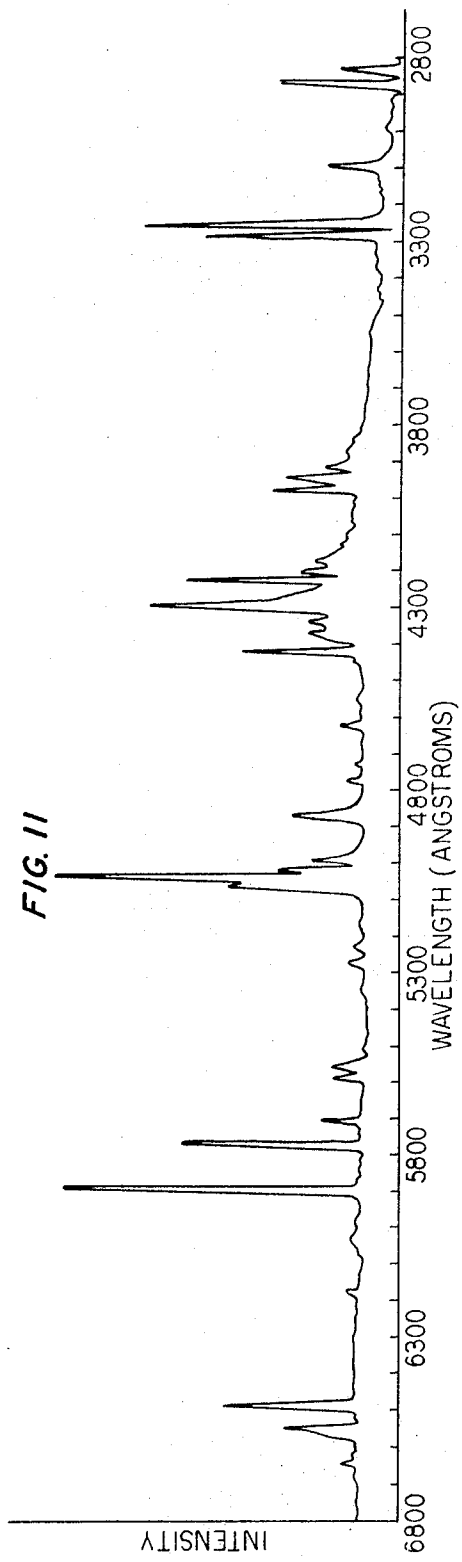

INTENSITY
6800
6300
5800
5300
4800
4300
3800
3300
2800
WAVELENGTH (ANGSTROMS)

FIG. 11


INTENSITY
6800
6300
5800
5300
4800
4300
3800
3300
2800
WAVELENGTH (ANGSTROMS)

METHOD OF ANALYZING A SOLID SURFACE FROM PHOTON EMISSIONS OF SPUTTERED PARTICLES

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a method and apparatus for analyzing solid surfaces by means of low-energy collisions with a low-density gaseous particle beam to produce characteristic spectra.

2. Prior Art

In the field of chemical analysis, a simple method for the nondestructive testing of solid surfaces has been long desired, but is still an elusive goal. For example, one recently developed technique involves focusing a laser beam on a small selected area of the surface to be analyzed so as to remove a portion of the surface by vaporization, thereby leaving behind a crater which may be large enough to be visible to the unaided eye. The vapor is subsequently analyzed spectroscopically. Another nondestructive test technique is sometimes referred to as hollow cathode discharge. Briefly, the principle of operation of hollow cathode and similar glow discharge apparatus is as follows. A potential is developed between an anode and a cathode in an inert gas atmosphere, e.g., Ne at 16 to 20 mm. of Hg; a glow discharge results from the collision and excitation of the gas with electrons. A sample placed near the cathode, e.g., inside a hollow cathode, gives up particles as a result of bombardment by the surrounding gas, and at least some of these particles are then free to participate in the glow discharge by collision with electrons. Knowledge of the surface may then be gained by an analysis of the glow discharge. However, in order that a significant portion of the glow discharge be due to particles from the sample surface, a relatively large amount of material must be removed from the surface. Such removal leads to large power consumption, and possible thermal damage to the sample.

The search continues for a simple and effective technique for the nondestructive chemical analysis of solid samples.

SUMMARY OF THE INVENTION

According to the invention it has been discovered that bombardment of solid surfaces with ion or molecule beams which may be of low energy and low density, results in the sputtering of excited particles directly from the surface. Resultant photon emissions from the sputtered particles in the vicinity of the surface are characteristic of the constituents of the surface and the intensities of the spectral peaks are related to the number of collisions, thus enabling identification of unknown constituents and their relative concentrations in the surface.

Devices of the invention are notable for their simplicity and are particularly useful in applications requiring low weight and low power consumption. According to a preferred embodiment, spectra are obtained by first directing an ion beam of nitrogen or a rare gas through an ion electrostatic lens into a sample chamber and against the surface to be analyzed, and then detecting resultant photon emissions over a preselected band of wavelengths using single photon counting techniques.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is a schematic diagram of a preferred embodiment of the inventive apparatus;

FIG. 2 is a graph of intensity versus wavelength for the photon emissions resulting from the collision of He^+ ions with a nickel surface;

FIG. 3 is a graph similar to the graph of FIG. 2 for the collision of N_2^+ ions with a nickel surface;

FIG. 4 is a graph similar to the graph of FIG. 2 for the collision of Ar^+ ions with a nickel surface;

FIG. 5 is a graph similar to the graph of FIG. 2 for the collision of N_2^+ ions with a copper surface; FIG. 6 is a graph similar to the graph of FIG. 2 for the collision of Ar^+ ions with a copper surface;

FIG. 7 is a graph similar to the graph of FIG. 2 for the collision of Ne^+ ions with a copper surface;

FIG. 8 is a graph similar to the graph of FIG. 2 for the collision of N_2^+ ions with a germanium surface;

FIG. 9 is a graph similar to the graph of FIG. 2 for the collision of Ar^+ ions with a germanium surface;

FIG. 10 is a graph similar to the graph of FIG. 2 for the collision of N_2^+ ions with a silicon surface;

FIG. 11 is a graph similar to the graph of FIG. 2 for the collision of Ar^+ ions with a silicon surface; and

FIG. 12 is a graph of excitation cross section versus ion energy for N_2^+ ions bombarding a nickel surface.

DETAILED DESCRIPTION OF THE INVENTION

For convenience, the method will be described according to a preferred embodiment. The first two steps of ion collection and ion focusing involve considerations and techniques well known to those skilled in the art of mass analysis. In general, however, it may be stated that the purpose of the collection and focusing steps is to present a sufficient number of ions to the collision surface at a sufficient rate to allow detection of any photon emissions which result. If the detecting means chosen is particularly sensitive, such as single photon counting means, then tolerable collection efficiency could, of course, in general be lower than required with less sensitive detection means such as photo diodes, scintillation devices or proportional counters. The next step of ion acceleration is critical to the obtaining of the low-energy collision-induced emissions. The acceleration step must in general produce ions having energies of at least 3 to 5 electron volts above the energy arrived at by the following equation:

$$E = E_s + \left(\frac{m_1 + m_2}{m_2}\right) E^*,$$

where

E_s is the threshold energy for the sputtering of surface atoms in their electronic ground states,

E^* is the excitation energy of a specific excited state of the sputtered atom,

m_1 is the mass of the incident ion or molecule, and

m_2 is the mass of the sputtered atom.

Standard excitation energies E^* are known, and are therefore not a necessary part of this description. They are obtainable, for example, in energy level tables published by the National Bureau of Standards. Likewise, threshold energies E_s are known for a number of ionic species incident on a variety of surfaces, but in any event are readily determinable by simple experimentation.

The energy of the ion beam may be as large as desired. However, it will ordinarily be preferred to have a beam energy of from 100 to 4,000 electron volts, below which the signal intensity resulting from the photon emissions is in general too low to be conveniently detected, and above which power consumption and probable destruction of the sample surface outweigh the advantage of increased signal intensity.

Where the surface to be analyzed exhibits a conductivity value which is low enough to permit significant charge buildup on the surface and resultant repulsion of incoming ions, charge buildup may be avoided by placing a conducting grid on the surface or in close proximity to it. The distance between the conducting members of the grid is, of course, not critical, but should be such as to allow a beam transmission of at least 40 percent and preferably for optimum signal intensities at least 80 percent. By way of example, copper grids having 25 lines per centimeter and a transmission of about 80 percent are commercially available.

The species chosen to collide with the sample surface must do so at a sufficient energy to sputter excited particles therefrom, and thus may be of any element except hydrogen, whose mass is in general insufficient to cause significant sputtering at low energies due to insufficient momentum transfers. Since at present it is most convenient to obtain collision particles of the proper energy by accelerating charged particles through an ion lens, it will ordinarily be preferred to choose

easily ionizable and relatively stable gases having substantial masses such as nitrogen and the rare gases, Ne, Ar, Kr, and Xe.

The pressure in the target chamber must be sufficiently low such that the intensity of photon emissions from sources other than the sample surface is negligible in comparison to the spectral peaks of interest. In general, a pressure in the target chamber of $\approx 5\times10^{-6}$ Torr or less will be required. This pressure is readily achieved by diffusion pumping. The beam current must be sufficient to provide the minimum number of collisions desired per unit of time and is thus determined by the ion collection efficiency, the intensity of the photon emissions and the sensitivity of the detection means. When using single photon counting techniques the number of collisions per unit of time may be as low as 10^4 per second.

It will ordinarily be necessary to obtain calibration spectra for the collision pairs of interest. Such procedure permits the unequivocal identification of unknown species and their relative concentrations in a solid sample surface by comparison of their spectra with the calibration spectra.

Referring now to FIG. **1** there is shown one embodiment of the inventive apparatus in which ion beam source **10** provides ions, aperture **11** collects the ions, ion lens **12** accelerates the ions to the proper energy while also focusing the ions into an ion beam **13** and directing the beam through aperture **14** into collision chamber **15** containing the sample **16** to be analyzed. The sample is positioned so that at least one surface is bombarded by the ion beam. Photons emitted as a result of the collisions pass through quartz window **17** and spectrometer **18** to a photomultiplier tube **19**. The electrical signals produced by the impact of photons on the photomultiplier tube are conducted through leads **20** to conventional signal processing equipment not shown where the counting rate is determined and registered. Chamber **15** may be evacuated through port **21**. Due to the fact that photon emissions from the sputtered particles originate within a continuous space from the sample surface to some distance away from it, typically 0.01–0.5 cm. at these energies, the position of the detection equipment is not critical.

The above-described apparatus is suitable for the obtaining of calibration spectra and also for obtaining spectra of samples whose constituents are not predictable. Where the identities of the constituents are suspected or known, it may be more convenient to replace the spectrometer with narrow band transmission filters so as to obtain photon counts for only the spectral regions of particular interest.

EXAMPLE 1

Using an apparatus similar to that shown in FIG. **1**, collisions were obtained for the 10 pairs and at the ion energy shown in Table I below, and the resultant photon emissions were detected over the wavelength ranges indicated.

TABLE I

Ion Acceleration Energy (3,000 ev.)

Wavelengths Detected (A.)	Collision Pair	Pair Number
2800–6600	He^+ and Ni	1
2800–6000	N_2^+ and Ni	2
2800–7800	Ar^+ and Ni	3
3200–6600	N_2^+ and Cu	4
3200–6600	Ar^+ and Cu	5
3200–6600	Ne^+ and Cu	6
3200–7800	N_2^+ and Ge*	7
3200–7800	Ar^+ and Ge*	8
2800–6800	N_2^+ and Si*	9
2800–6800	Ar^+ and Si*	10

Conducting grids were placed over these sample surfaces

Results are depicted graphically as emission spectra in FIG. **2**, **3**, **4**, **5**, **6**, **7**, **8**, **9** and **10**, respectively, for the pairs listed in the table. The intensity of photon emissions (arbitrary units) is plotted versus wavelength (angstroms) in each figure. In FIG. **2** the intensity peaks at about 3,900, 4,300, 5,900 and 6,570 A are attributable to sources other than the Ni surface, such as source radiation and surface contaminants. The remaining peaks including those at about 3,000, 3,050, 3,100, 3,240, 3,380, 3,390, 3,415, 3,461, 3,519, 3,570 and 3,620 A, are substantially attributable to Ni. In FIG. **3** the intensity peaks at about 3,900, 4,300 and 5,900 A are attributable to sources other than the surface. The remaining peaks including those previously mentioned and also including those at about 3,680, 4,080, 4,220 and 4,600 A are characteristic of the nickel surface.

In FIG. **4** is shown the spectrum for pair number 3. The peaks at about 4,300 A and 6,580 A are attributable to sources other than the Ni surface, while the remaining peaks including those mentioned for FIG. **2** and **3** above are generally characteristic of the Ni surface.

In FIG. **5** is shown the spectrum for pair number 4. The intensity peaks at about 3,250 A and 3,270 A and their second order counterparts at about 6,500 A and 6,540 A are attributable to copper. The peak at 5,000 A is tentatively attributed to copper, and the remaining peaks are due to other sources.

In FIG. **6** and **7** are shown the spectra for pair numbers 5 and 6. The four intensity peaks for copper pointed out above for pair number 4 are again evident. Other peaks are attributable to other sources.

In FIG. **8** and **9** are shown the spectra for pair numbers 7 and 8, respectively. The intensity peaks at about 7,680 A and 7,700 A are attributable to germanium. The peaks between 3,200 A and 3,600 A are tentatively attributed to germanium, while the remaining peaks are due to other sources.

In FIG. **10** and **11** are shown the spectra for pair numbers **9** and **10**, respectively. The peaks for copper are evident in these spectra, since a copper grid was placed over the sample surface prior to bombardment. These peaks occur at about 3,250, 3,275, 6,500 and 6,550 A. The peaks at about 2,880, 4,440, 4,870, 5,015, 5,035, 5,055 and 5,770 A are attributable to silicon. The peaks at about 3,365 A and those from about 5,550 to 5,720 A are tentatively attributed to silicon. The remaining peaks are due to other sources.

EXAMPLE 2

Using an apparatus similar to that shown in FIG. **1**, collisions were obtained for an N_2^+ ion beam on a nickel surface over the ion acceleration energy range of from about 20 to 3,000 electron volts. The excitation efficiency was measured over the wavelength range of about 3,365 to about 3,375 A.. The excitation efficiency may be defined as the number of photons emitted per incident ion. The results are shown in FIG. **12** where excitation efficiency or cross section is plotted on the vertical scale (in arbitrary units) against ion acceleration energy. It may be seen from the figure that excitation efficiency increases abruptly from a low value at about 50 electron volts and continues to increase rapidly to about 200 electron volts, beyond which it gradually decreases as a function of energy. The steep sloped region at about 50 electron volts may be termed the excitation threshold for the nickel surface and is characteristic thereof. It will thus be appreciated that determination of the characteristic excitation threshold presents an additional technique for the identification of solid surfaces.

The invention has been described in terms of a limited number of embodiments. Other embodiments are contemplated. For example, since it is the function of the collision particles simply to produce sputtered particles of the surface constituents in an excited state, the ion beam described may be replaced by a beam of neutral particles provided, of course, these particles collide with the surface at the requisite ener-

gies. In such a case, the problem of repulsion of the beam by a charged sample surface is in general substantially avoided.

While the gaseous particles have been described as forming a beam, it will be appreciated that the particle distribution in the sample chamber may be such that a "beam" is not differentiable in the ordinary sense, and yet sufficient collisions be obtained to allow the practice of the invention.

What is claimed is:

1. A method for determining the identities and relative concentrations of constituents of a solid surface comprising:

1. producing collisions of incident particles with the solid surface with sufficient energy to sputter particles from the surface, in an excited state to obtain photon emissions from at least a portion of said sputtered particles;
2. detecting at least a portion of the photon emissions so as to obtain electrical signals; and
3. processing the signals so as to obtain at least a portion of a characteristic spectrum, the wavelengths at which spectral peaks occur indicating the identity of the constituents, and the intensities of the peaks indicating the relative concentrations of the constituents;

characterized in that said incident particles are in the form of a beam.

2. The method of claim 1 in which the collisions occur at an energy of at least 3 to 5 electron volts in excess of the energy defined by the relationship

$$E = E_s + \left(\frac{m_1 + m_2}{m_2}\right) E^*,$$

where m_1 is the mass of the incident ion or molecule, m_2 is the mass of the sputtered atom, E_s is the threshold energy for the sputtering of surface atoms in their electronic ground states, and E^* is the excitation energy of a specific excited state of the sputtered atom.

3. The method of claim 2 in which the collision occurs at an energy of from 100 to 4,000 electron volts.

4. The method of claim 1 in which the particle beam consists of ions of a member selected from the group consisting of nitrogen and the rare gases helium, neon, argon, krypton and zenon.

5. The method of claim 1 in which the solid surface is contacted by a conducting grid.

6. The method of claim 1 in which a conducting grid is positioned adjacent the solid surface.

* * * * *