to a change in electronic configuration ($\eta^5 \rightarrow \eta^3$ transformation) which might be required to be associative mechanism.

A proposed reaction profile for Cp(C_5H_7)CrCO is shown in Figure 3. This proposed reaction profile determined for CO substitution reaction mechanism of Cp(S-C_5H_7)CrCO is allowed by the quantitative changes of the reaction coordination. The energy of [Cp(U-C_5H_7)Cr]$^{\neq}$ transition state is about 4.25 kcal/mole lower than the of [Cp(S-C_5H_7)Cr]$^{\neq}$ transition state, and no significant energy barrier is found in the η^5-S $\longleftrightarrow$ η^5-U interconversions. The [Cp(U-C_5H_7)Cr]$^{\neq}$ mechanism will be favored over [Cp(S-C_5H_7)Cr]$^{\neq}$ mechanism, and this result is agreed with the experimental result. Therefore, it is suggested that the 18-electron Cp(C_5H_7)CrCO undergoes CO substitution by a predominantly dissociative mechanism, involving the following conformation: η^5-S $\longleftrightarrow$ η^5-U interconversions.

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A Linear Photodiode Array Detector System for Multichannel Spectroscopic Applications

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A multichannel optical detector system employing a self-scanning linear photodiode array has been developed. The photodiode array detector system is designed for various applications which require fast, multichannel detection of transient signals. The detector system consists of a controller which runs on an IBM personal computer and a detector head connected to the controller through a DB-15 cable. The entire scanning of 1024 detector elements is achieved in 20 ms. By using an on-board 16-bit counter/timer, the operational mode of the photodiode array detector is fully programmable by software. The design considerations and the performance of the photodiode array detector system is presented.

Introduction

Numerous modern analytical techniques are based on detection and quantization of light in the UV to near IR regions of the spectrum. Also, the rapid acquisition of spectral data continues to be an important objective of the spectroscopist, not only for reasons of efficiency but also for enhanced information. For instance, spectral data obtained in a minute is of no kinetic value if the half-life of the monitored reaction is a millisecond. Recently, revolutionary developments in multichannel detectors have greatly expanded and improved the capabilities of current spectrochemical techniques[1].

Solid state image sensors such as photodiode array (PDA)[2], charge-coupled device (CCD)[3], and charge-injection device (CID)[4] have been regarded as highly-technical, expensive, and difficult to use optical detectors. However, recent advances in solid state technology and computer science made these devices find their ways more and more into various scientific instruments. The advantages of solid state image sensors compared to other detectors are that they are high speed, multichannel, and integrating detectors. Many hundreds of data points can be recorded in one single reading, permitting rapid acquisition of spectra. Photodiode arrays are excellent for taking a sequence of scans of rapidly changing transient signals. Conventional mechanical scanning systems usually lack sufficient speed to adequately perform such tasks.

Solid state image sensors are large scale integrated circuits fabricated on a single monolithic silicon crystal[5]. The device consists of an array of hundreds of detector elements, each acting as a light-to-charge transducer, a storage device, and an electronic scanning circuitry. The spectral response of a photodiode array is that of silicon, about 180 nm to 1100 nm which is a wider range than photomultiplier tube (PMT). The quantum efficiency of silicon photodiodes is higher than PMT. The quantum efficiency of photodiode array detector is approaching to 80% in the visible region and 40% in the UV region[6]. It is also important to understand that PMTs and photodiode arrays measure light differently. Photomultiplier tubes measure the instantaneous light intensity (power), while photodiode arrays measure the total light energy over the time of exposure. Noise can be reduced by integration because the signal level is raised to the square of the number of measurements N while noise level is proportional to the square root of N.

There are several commercial instruments which employ solid state image sensors as multichannel detector. Commercial photodiode array spectrophotometers have low wavelength resolution and accuracy, are limited by their design in extendibility. Most of commercial multichannel detectors are still expensive and require extensive modifications to be used for various applications. The construction of an inexpensive photodiode array spectrometers has been reported in the literature.[7,8] However, these systems still require robust equipments and modifications to use. The photodiode array detector system described here attempts to solve these problems. The photodiode array detector system runs on inexpensive personal computers and the operation of the detector is programmable to provide flexibility and extendibility. It is designed for various applications which require low cost and high performance optical detector.

Experimental Section

Materials and Equipment. Electronic circuit design and printed circuit board (PCB) were made using an electronic CAD system, P-CAD (Ver. 4.02, Personal CAD systems). For instrument control and data analysis, programs were written with Turbo Pascal (Ver. 5.0, Boland International) and assembly language subroutines were incorporated for fast program execution. For spectroscopic applications, a spectrograph, a fiber optic cable, and a mercury lamp were purchased from Oriel corporation (Stratford, CT). A photodiode array detector (RL1024SAQ) with quartz window for UV detection was purchased from EG&G Reticon (Sunnyvale, CA). This detector has 1024 active detector elements and each element size is 25 μm×2.5 mm, which is suitable for 100 : 1 aspect ratio slits used in most spectrographs. The grating used is blazed 400 nm with 400 lines/mm groove spacing.

Instrumentation. The photodiode array detector system consists of two parts, a controller card which sits on an expansion slot of an IBM-PC or compatible systems and a detector head which is connected to the controller through a DB-15 cable. The major functions of the controller board are the synthesis of control signals necessary for driving the PDA and the digitization of spectral signal. The functional block diagram of the controller and detector head is shown in Figure 1. The analog-to-digital converter (ADC) was a 12-bit resolution AD674 (Analog Device) with 10 μs conversion time. A 16-bit programmable counter/timer (8254, Intel) was used to generate control signals for PDA with a 1 MHz clock source. Although the PDA used can run at the maximum speed of 250 kHz, the ADC speed limits the scanning speed of the PDA to 20 μs per detector element. The PDA detector head board extracts spectral signal by taking difference between the active and the dummy signals to reduce the switching transient noise. After conversion of the video charge signal into corresponding voltage signal, a programmable instrumentation amplifier (AD524, Analog Device) is used to obtain the desired signal gain.

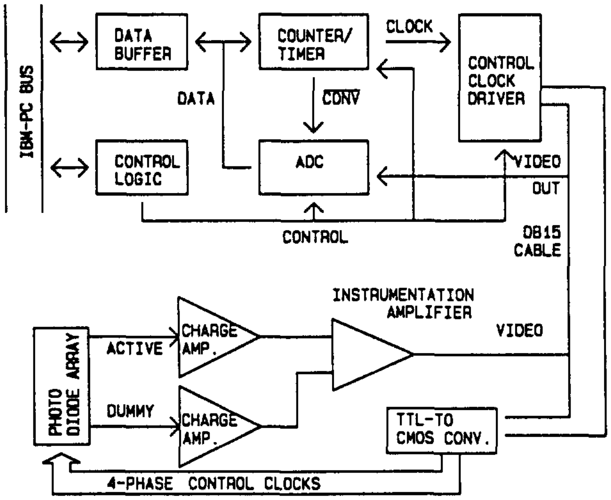

Figure 1. Block diagram of the photodiode array detector system.

Results and Discussion

In terms of the amount of information obtained in a single observation, spectroscopic techniques can be classified into single and multichannel detection techniques. Multichannel detection techniques significantly broaden the scope of spectroscopy and allow for many scientific developments which have been paced by detection limitations such as multicomponent analysis of microsamples, rapid kinetic studies with up to 2000 spectra/s, observations of short lived signals as in fluorescence or chemiluminescence and Raman laser spectroscopy, and diagnostic studies of plasmas and low light-level astronomical spectroscopy.

Ideal multichannel detection system for spectroscopic applications should exhibit following characteristics; simultaneous integration of multiple wavelengths, wide spectral coverage with adequate resolution, high and uniform spectral response, high signal-to-noise (S/N) ratio, large dynamic range, linear response, flexible channel addressing, rapid spectral data readout, stability and reliability, durability and reasonable cost. Solid state image sensors incorporate many

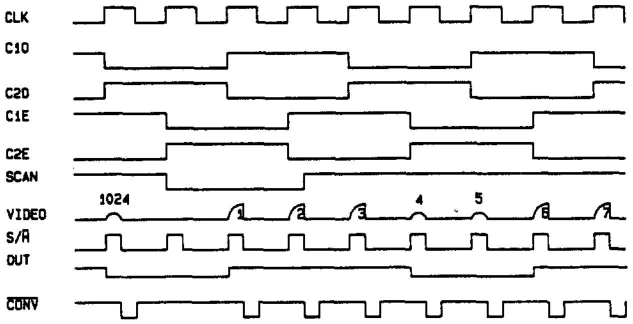

Figure 2. Timing diagram of the photodiode array detector controller.

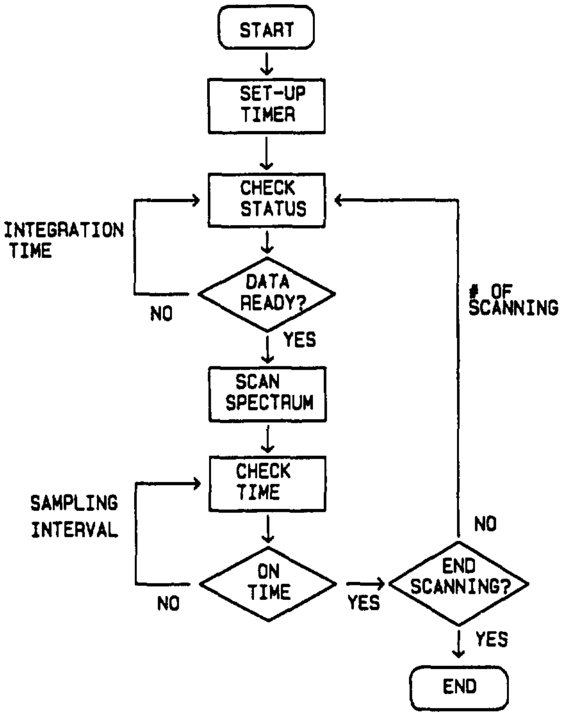

Figure 3. Software flowchart for the photodiode array detector system.

of these characteristics and appear to be the multichannel detector with the best prospects for extensive use in the future.

The control signals were synthesized by using a programmable counter/timer, Intel 8254. The counter/timer has three 16-bit channels and runs at 1 MHz. The big advantage of using a programmable counter/timer is that the operational mode of the PDA is fully programmable by software which is very convenient when the operational parameters are to be changed as the experimental conditions are changed. The timing diagram of the control signals for driving the PDA is shown in Figure 2. The PDA used is a linear type and requires 4-phase control clock signals. The master clock pulse width is 10 μs. The 4-phase clock signals were obtained by dividing the master clock by four. At the rising edge of each 4-phase clock signals the video signal exits as a train of 1024 analog pulses. Therefore, a sample-and-hold (S/H) was used to hold the video signal at the signal peak unitl the ADC completes conversion. After the ADC status goes low the digitized video data are transferred into memory for further processing. The integration time of the PDA is the time interval between the scan start pulses. Therefore, the minimum integration time must be longer at least four master clock cycles than the scanning time required for single frame of 1024 detector elements.

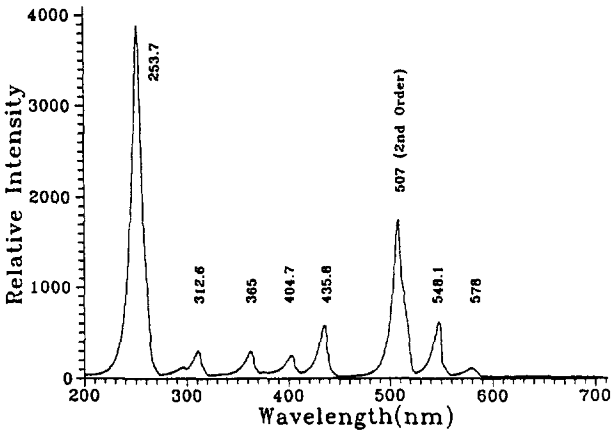

Figure 4. Spectra of emission of a Hg(Ar) lamp obtained with the photodiode array detector.

The software flow diagram for the PDA operation is shown in Figure 3. The scanning of the 1024 spectral data was done with a assembler subroutine for speedy execution. To start the PDA scanning the counter/timer must be programmed first to generate the master clock and the scan initiation signal whose time interval corresponds to the integration time. The controller was designed so that the scanning interval and the integration time may be different. This feature allows the user to scan PDA at any time with a fixed integration time. The scanning of the entire 1024 PDA data was complete in 20.48 ms.

The spectral response of the PDA detector was tested using a spectrograph combined with a fiber optic cable. The spectrograph contains a flat-field grating which is blazed at 400 nm with 400 lines/mm grove spacing. The PDA detector head was placed at the spectrograph exit port and a Hg(Ar) lamp was used as a calibration line source with 25 μm entrance slit. The spectrum of the Hg(Ar) lamp showed characteristic peaks from 200 nm to 712 nm as shown in Figure 4. The spectrum was obtained with integration time of 50 ms and the signal amplification of 10. The PDA showed a strong peak at 253.7 nm in the UV region with a second order peak at 507 nm. From these two characteristic peaks the spectrograph with PDA was calibrated. It was found that the spectrograph showed very accurate linear reciprocal dispersion over the exit slit and each photodiode detector element cover 0.5 nm of the exiting spectrum. Therefore the PDA detector can cover spectrums in the 200-712 nm wavelength range with 0.5 nm resolution.

The PDA is an integrating detector. The incident light on the PDA is accumulated into each storage capacitor and the amount of accumulated charge is directly proportional to the intensity of the incident light and the integration time. To test the influence of the integration time on the observed signal intensity, the PDA was exposed to Hg(Ar) lamp and

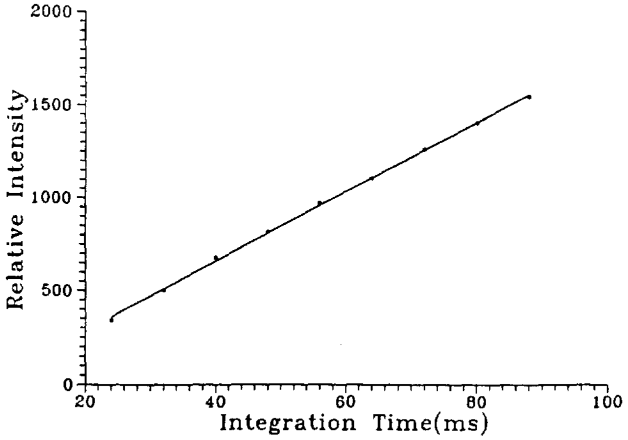

Figure 5. The effect of integration time on the photodiode array detector signal amplitude.

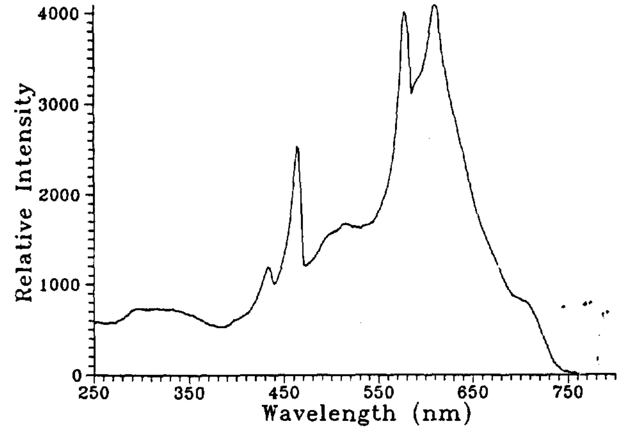

Figure 6. Captured output spectrum of a fluorescent lamp. The uncorrected spectrum was obtained with 100 μm input slit.

the intensity of a fixed detector element which corresponds to a peak at 507 nm was measured as changing the integration time from 24 ms to 100 ms. The intensity of the PDA was linearly proportional to the integration time as shown in Figure 5. A slight deviation from the origin of the intensity-time plot was due to the unmatched transitor and resistor pairs used for active and dummy analog signal circuit.

The high speed of the PDA spectrometer enables to obtain a time-resolved spectrum which is essential in reaction kinetic studies and transient signal detection. To further test the instrument the PDA spectrometer was exposed to the fluorescent room light and its spectrum change was monitored. The spectrum showed strong peaks in the visible region from 450 nm to 650 nm with a little background from 250 nm to 380 nm as shown in Figure 6. The PDA was programmed to capture the spectrum 15 times for a minute and the captured spectrum was shown in Figure 7. The fluctuations of the fluorescent lamp were clearly seen in the time-resolved three dimensional plot of the obtained spectrum.

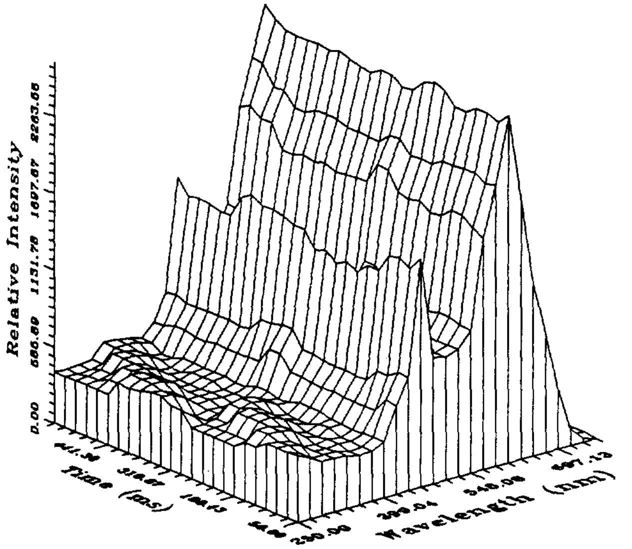

Figure 7. Three dimensional plot of a uncorrected emission spectrum of a fluorescent lamp.

The PDA contains a number of switching field-effect-transistors (FETs) in its internal structure. This generates a fixed pattern noise when the PDA starts scanning. The video signal was obtained by taking the differential signal between the sensing (active) and the dummy diodes to remove the fixed pattern noise. However, it was difficult to completely remove the fixed pattern noise especially when the incident light signal is low and the signal amplification is high. It was found that the long integration time is better than the higher gain amplification of the signal for the reduction of the fixed pattern switching noise.

Conclusions

A versatile photodiode array detector system was developed for spectroscopic applications. The instrument developed can be used for various purposes using an IBM-PC or compatible personal computers. The photodiode array detector contains 1024 detector elements and scans the entire detectors in 20 ms so that a rapid spectroscopic data processing is possible. The controller of the PDA was designed using a high speed programmable counter/timer, which enables a versatile operation by the user. The fixed pattern noise reduction and the sensitivity enhancements are the current challenges of the PDA but it will be achieved soon as the microelectronics technology develops. It is expected that the solid-state image sensors will replace the conventional single channel detectors for multichannel analytical instruments in the near future.

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Isomorphous Substitution of Fe in Sodalite and Its Electric Characterization

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Experiment on isomorphous substitution of Al by Fe in sodalite framework was carried out using dry way method at 800-900℃ in nitrogen atmosphere. The substitution of Fe was possible up to 25 mole% with some deviation of symmetry in sodalite cage. The cubic unit cell parameter increased with increasing Fe content. It showed ionic semiconducting property, especially the highest conductivity and the lowest activation energy in 10 mole% Fe-substituted sodalite which could behave as a superionic conductor at above 400℃. When more Fe was introduced into sodalite the electronic conductivity was improved at high temperature. But the relative electronic contribution was found to be lower compared with ionic contribution at high temperature. In infrared spectra some major absorption bands of sodalite shifted to lower wave numbers due to heavier Fe atoms substitution in Al lattice sites.

Introduction

The structure of sodalite ($Na_8Al_6Si_6O_{24}Cl_2$) is known to be cubic p$\bar{4}$3m[1]. As shown in Figure 1(b) its unit cell consists of 14-hedron with eight 6-rings and six 4-rings where Si and Al tetrahedra are linked together alternately. It is called a cubooctahedron or sodalite unit cell. The cubooctahedron is the basis for the structure of sodalite in Figure 1(a) which is obtained by directly connecting such 14-hedra through sharing of the 4-membered rings. The free diameter of a sodalite unit is about 6.6 Å[2]. Here the free distance means the distance between diagonally opposite points of polyhedra which is not impinged upon by the oxygen atom linings. The channel networks in sodalite allow 3-dimensional diffusion of all guest molecules small enough to enter the main cavities. The guest molecules and framework oxygens are not hard spheres and the lattice oxygens are also in the state of vibration with breathing frequencies.

In a previous study it has been reported that the elements of Be, B, Fe, Cr, P, and Mg can replace other elements such as Al and Si in tectosilicates[3]. The substitution of Al by Fe in the ZSM-5 framework has also been established[4-6]. In another study Szostak and Thomas were the first to synthesize a condensed phase zeolite, sodalite with significant quantities of iron in the framework ($SiO_2/Fe_2O_3=6-30$)[7].

In tectosilicates trivalent aluminum has inert valence electrons. On the other hand, trivalent iron has $3d^5$ electrons which might show good electronic characters. In an effort to elucidate the role of Al site substitution by Fe on the electronic properties of sodalite, a study was undertaken to prepare the samples by dry way synthetic method in high temperature condition. Because salts are relatively non-volatile and high melting, dry way synthesis of salt-bearing tectosilicates can be expected from salt melt and silica, alumina, and alkali. Sodalite has open structure and thus the mobility

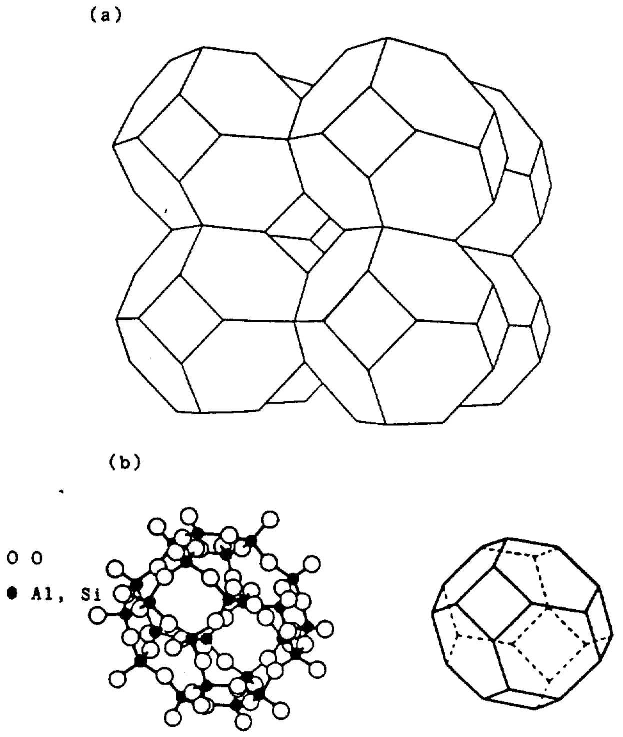

Figure 1. (a) The stacking of 14-hedra of sodalite structure, (b) Sodalite unit.