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Electrochemical Formation of ZnS Screens

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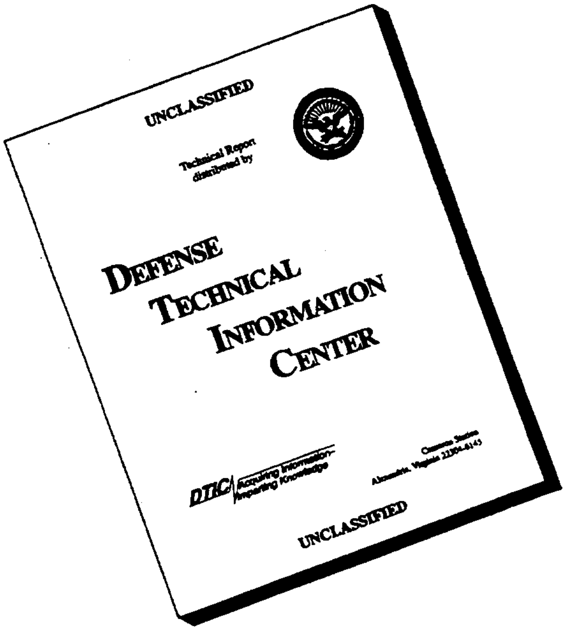

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This paper is a preliminary report on the formation of ZnS thin films thicker than 5 monolayers using electrochemical atomic layer epitaxy (ECALE). This films were electrodeposited on Au coated Si wafers and ITO coated borosilicate glass slides. The deposit's morphology was examined by scanning electron microscopy and composition was determined by electron probe microanalysis. Grazing angle X-ray diffraction showed cubic (111) ZnS films.

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Abstract

This paper is a preliminary report on the formation of ZnS thin films thicker than 5 monolayers using electrochemical atomic layer epitaxy (ECALE). Thin films were electrodeposited on Au coated Si wafers and ITO coated borosilicate glass slides. The deposit's morphology was examined by scanning electron microscopy and composition was determined by electron probe microanalysis. Grazing angle X-ray diffraction showed cubic (111) ZnS films.

Keywords: ECALE, electrochemistry, ZnS, thin films, phosphors

Introduction

Our group has been developing the electrochemical atomic layer epitaxy (ECALE) methodology in hopes of achieving greater control of composition, morphology, and structure in the electrodeposition of II-VI compounds [1-4]. ECALE is the electrochemical analog of atomic layer epitaxy (ALE) which is a methodology developed for the formation of materials one atomic layer at a time. Generally, ALE is performed in vacuum using metallorganic molecular beam epitaxy or in a chemical vapor deposition gas-phase reactor where atomic layers of the elements constituting a compound are deposited individually by surface limited reactions.

In ECALE, elements are alternately deposited, one atomic layer at a time, using the electrochemical phenomena known as underpotential deposition (UPD) [5-7]. UPD occurs when one element deposits on a second element at a potential prior to (under) that necessary for the element to deposit on itself, due to the energetics of compound formation. In forming ZnS the Zn is deposited using reductive UPD,

$$Zn^{2+} + 2e^- = Zn_{(UPD)} \qquad [1]$$

and S by oxidative UPD

$$S^{2-} = S_{(UPD)} + 2e^-. \qquad [2]$$

Our initial studies [8] used a static thin-layer electrochemical cell (TLE) to determine initial deposition conditions. However, the manually operated TLE system was exceedingly tedious after more than 5 monolayers of compound deposition. As a result, an automated deposition system has been constructed and used to form deposits of CdTe, CdS, and ZnS with the ECALE methodology. Initial incarnations of the automated system used a thin-layer flow cell which proved problematic [9]. A thicker cell design based on a common "H-cell" is now in use and results in much more reproducible deposits.

Previous studies of the ECALE method have indicated a number of important variables affecting deposit morphology, stoichiometry, and structure. The most critical variable is the elements' deposition potential. Electron probe microanalysis (EPMA), scanning electron microscopy (SEM), field emission scanning electron microscopy (FESEM), and thin layer X-ray diffraction (XRD) have been used to characterized the deposited films.

Experimental

A diagram of the deposition system constructed in our lab for applying ECALE methodology is shown in Figure 1A. The system consists of solution reservoirs, peristaltic pumps, distribution valve, actuator, potentiostat, and electrochemical cell. The valves, pumps and potentiostat are all interfaced to a PC with a PCL-711S lab card from Advantech (San Jose, Ca.). The actuator is a Smart Valve Actuator by Thar Designs, Inc. (Pittsburgh, Pa.) that uses RS232 protocol for communication with the PC.

The design of the system involved the use of one pump for each solution line. The tubing consisted of tygon peristaltic tubing (0.125" OD, 0.11" ID) which was fitted into 0.125 in. OD., 0.067" ID PEEK with PEEK 14/28 finger tight fittings. The tygon and PEEK tubing were chosen for their low oxygen permeability. Tubing was kept as short as possible in order to minimize solution residence time and any associated exposure to oxygen. Solution exchange was facilitated using a central, inert, rotatable distribution valve (VICI, Upchurch Inc., Hamilton Inc.) which has minimal internal volume, mounted on the actuator. The electrochemical cell is a H-Cell modified to allow solution in and out (Figure 1B).

Both Au on Si and ITO coated borosilicate glass have been used as substrates. The Si (100) wafers were purchased from International Wafer Service (Portola, Ca.) and sent to EMF Corporation (Ithaca, N.Y.) for coating with 200 nm of Au. A 5 nm buffer layer of Cr was used between the Au and Si. The borosilicate glass slides were coated with 300 nm of ITO by Thin Film Devices, Inc. (Anaheim, Ca.) with a sheet resistance of 10 ohms/square. Before each deposition experiment, the substrates were alternately rinsed in water and in acetone 3 times, ending with a rinse in water.

Solutions were prepared with 18 M Ω-cm water from a Barnstead NANOpure water filtration system, fed with the departmental deionized water supply. All solutions had 0.5 M $NaClO_4$-H_2O added as a supporting electrolyte. The S^{2-} solution was made with 5 mM Na_2S-$9H_2O$, pH = 11. The S blank solution pH was adjusted with NaOH. The Zn^{2+} solution was made with 5 mM $ZnSO_4$-$7H_2O$ and 50 mM acetic acid buffer, pH = 5.7. The Zn blank solution was a 50 mM acetic acid buffer, pH = 5.7. For our studies involving dopant species solutions were made in two ways. In case one, dopant species were added directly to the Zn^{2+} solutions using 1 mM $CuSO_4$-$5H_2O$, 1 mM $Mn(NO_3)_2$-XH_2O, or 0.1 mM Ag (dissolved in a minimal amount of concentrated HNO_3). Case two used separate 5 mM solutions of dopant species made with the same solution composition as the Zn^{2+} and Zn blank solutions. The potentiostat was built in-house using a conventional op-amp based design. All potentials are reported versus a Ag/AgCl (1 M NaCl) reference electrode.

A Jena Jenavert optical microscope was used for visible inspection of the deposits. SEM micrographs were taken on either a Philips 505 equipped with EDAX energy dispersive X-ray detectors or FESEM. EPMA was performed on a JEOL JXA-8600 superprobe, equipped with four-wave length dispersive X-ray spectrometers and an energy dispersive detector. An undoped ZnS single crystal was used as standard to calibrate the microprobe and the $\Phi(\rho z)$ program was used for signal correction. A Sintag 2000 diffractometer equipped with a liquid nitrogen-cooled, intrinsic, germanium solid state detector and a normal-focus copper X-ray tube powered at 40 mA, 40 KeV was used for XRD studies. Grazing angle scans were done using a thin film attachment.

Results/Discussion

Initial studies of ZnS deposition by ECALE involved use of a static thin-layer electrochemical cell (TLE) to manually deposit 1-5 cycles, and then electrochemically stripping the deposits to determine the total amounts of Zn and S [8]. The net result was a set of Zn and S deposition potentials that could be used in an initial ECALE cycle for studies with the automated system (Figure 2). The cycle begins with three rinses of S blank solution at -1.0V to condition the cell and tubing prior to the introduction of the S^{2-} solution. The S^{2-} solution is then rinsed in twice at open circuit. Open circuit is used to avoid depositing most of the S at the cell's entrance where the solution first encounters the substrate. Before draining the second S^{2-} rinse, the potential is stepped to -1.0V and held for 30 seconds. The S blank solution is then rinsed in three times to remove any remaining S^{2-} and three times with Zn blank to condition the cell before the introduction of the more acidic Zn^{2+} solutions. The Zn^{2+} solution is rinsed in twice at open circuit and then held while the potential is stepped to -0.9V for 30 seconds. Finally, the cell is rinsed three times with the Zn blank solution at -0.9V in order to rinse out any remaining Zn^{2+} ions. This is followed by the introduction of the S blank solution, initiating the next cycle.

Initial deposits of ZnS films were formed on ITO coated glass slides. EPMA data for these samples showed an average Zn:S ratio, after 200 cycles, of 1.35. The high Zn coverage appeared due, in part, to the way the deposition potentials were chosen. As stated above, our initial potentials were based on a study using a TLE, with a Au electrode. Optimum deposition potentials could easily vary for deposits formed in a thick layer cell compared with a thin layer cell.

If the Zn:S ratio is plotted versus the number of cycles (Figure 3), the ratio varies greatly with a low of 0.84 at 50 cycles and levels off at 1.47 after 150 cycles. Ideally, the plot should show a ratio of 1.00, regardless of how many cycles have been completed. When the relative intensities of Zn and S from EPMA are plotted versus the number of cycles (Figure 4), a nonlinear response is evident. If the film grew epitaxially, layer by layer, the graph should have been linear. The behavior, seen in Figure 4, is reminiscent of previous work with CdTe deposition [9], where particles and 3D nucleation sites resulted from a conproportionation reaction between Te^{2-} and $HTeO_2^+$, as well as a cross contamination problem within the valves that were used. These extra particles increased the overall surface area, resulting in an exponential increase in coverage with the number of cycles. In the present studies, conproportionation should not have been a factor, however, it is possible that some cross contamination was present. The hardware has been greatly improved with regards to cross contamination, but it is still an area of active research.

SEM micrographs of ZnS deposits made with 150 cycles, on ITO, at a magnification of 5700x (Figure 5A) shows a high density of particles covering the surface. At a higher magnification of 45,600x (Figure 5B), the particles appear like small balls on the surface. Again, these deposits resemble CdTe surfaces for which cross contamination was a major problem [9]. In this case, the polycrystalline nature of the ITO probably contributes a large density of nucleation sites. The deposition potentials play a very important role in determining the type of deposit obtained, and it is probable that much more work needs to be performed in optimizing those for Zn and S. If bulk zinc is depositing then three dimensional growth can be expected.

For deposits formed on Au coated Silicon (100) substrates, the EPMA Zn:S ratio for a 200 cycle deposit, formed under the same conditions as the initial ZnS on ITO films, was 1.06. The improvement of the Zn:S ratio may have to do with the increased crystallinity of the Au substrates which showed a preferred (111) orientation with XRD (Figure 6). Examination with SEM also shows smooth, even films with few particulates. However, further examination with FESEM (Figure 7A) at 100,000x magnification shows a surface covered with 25-50 nm nodules. This surface is very similar to the clean substrate surface (Figure 7B), which is consistent with an epitaxial growth mode. XRD (Figure 8) of a ZnS film on Au shows only a cubic (111) peak in the range of 23 to 33 degrees. No peaks due to hexagonal ZnS were evident.

Doping of the ZnS films on Au substrates were attempted by two methods: codeposition of the dopant and Zn from the same solution or insertion of individual atomic layers of the dopant by replacing the Zn^{2+} solution with a dopant solution, every 10th ECALE cycle. Cu, Mn, and Ag were used as dopants. In all cases, except with codeposition of Ag, EPMA failed to detect any dopant, indicating that the total amounts of dopants were below the instrument's detection limit. In the case of Ag codeposition, a Zn:Ag ratio of 4.30 was detected with a (Zn+Ag):S ratio of 1.07. There is clearly too much Ag present in the film, suggesting that much more dilute Ag solutions be used in the future. Examination of SEM micrographs (Figure 9) of the doped samples indicates that they were essentially smooth films with few particles (the particle in Figure 9 was used for focusing), much like the undoped ZnS films; no degradation due to doping is apparent. SEM of codeposited Mn doped ZnS films (Figure 10A) on ITO show the same particle like morphology as the original ZnS on ITO deposits (Figure 5A), at 5700x magnification, although the particles are larger. At magnification of 45600x (Figure 10B) the same ball like structure is seen as well (as in Figure 5B), although doping seems to have resulted in a larger grain size. XRD shows the same cubic (111) structure for both the Ag (Figure 11A) and Mn (Figure 11B) doped samples on Au. The Ag doped film seems to show a lower crystalline quality as compared to the Mn doped sample. This is expected with such a high content of Ag in the film compared to undetectable amounts of Mn. We were unable to obtain XRD on the deposits formed on ITO. Figure 12 is of the cathodoluminescence obtained from the ZnS:Mn on ITO sample at 10 KeV and 0.4 μA. The peak at 550 nm is consistent with Mn doping, but the count rate is very low.

Conclusions

An automated deposition system has been designed, built, and is being used to form ZnS thin films by ECALE methodology. Deposits up to 200 cycles have been formed on both ITO and Au on Si substrates. ITO substrates show a nucleated surface, possibly due to ITO's polycrystalline nature, while Au deposits on the substrates showed an improved, smoother morphology. Doping of films was attempted. The best results appeared to be those where the ZnS was doped with Mn. At present, it is clear that more work is needed, both to optimize the conditions for ZnS deposition and to improve the doping conditions.

Acknowledgments

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Figures

Figure 1A: Diagram of the electrochemical deposition system. All hardware is controlled by a computer to automate the deposition process.

Figure 1B: Diagram of modified H-Cell and distribution valve.

Figure 2: Pictorial representation of a typical program used in ECALE of ZnS. See text for detail.

Figure 3: EPMA ratio of Zn:S in series of ZnS deposits formed by an increasing number of ECALE cycles with the automated system on ITO substrates.

Figure 4: EPMA showing the relative intensities of Zn and S in a series of ZnS deposits.

Figure 5: SEM of a ZnS film deposited by 200 ECALE cycles on ITO. A) At a magnification of 5700X. B) At a magnification of 45600X.

Figure 6: Glancing angle XRD of 200 nm of Au deposited on a Si (100) wafer with a 5 nm Cr buffer layer.

Figure 7: A) FESEM of 200 ZnS ECALE cycles on Au coated Si substrate at a magnification of 100000x. B) FESEM of a clean Au coated Si substrate at a magnification of 100000x.

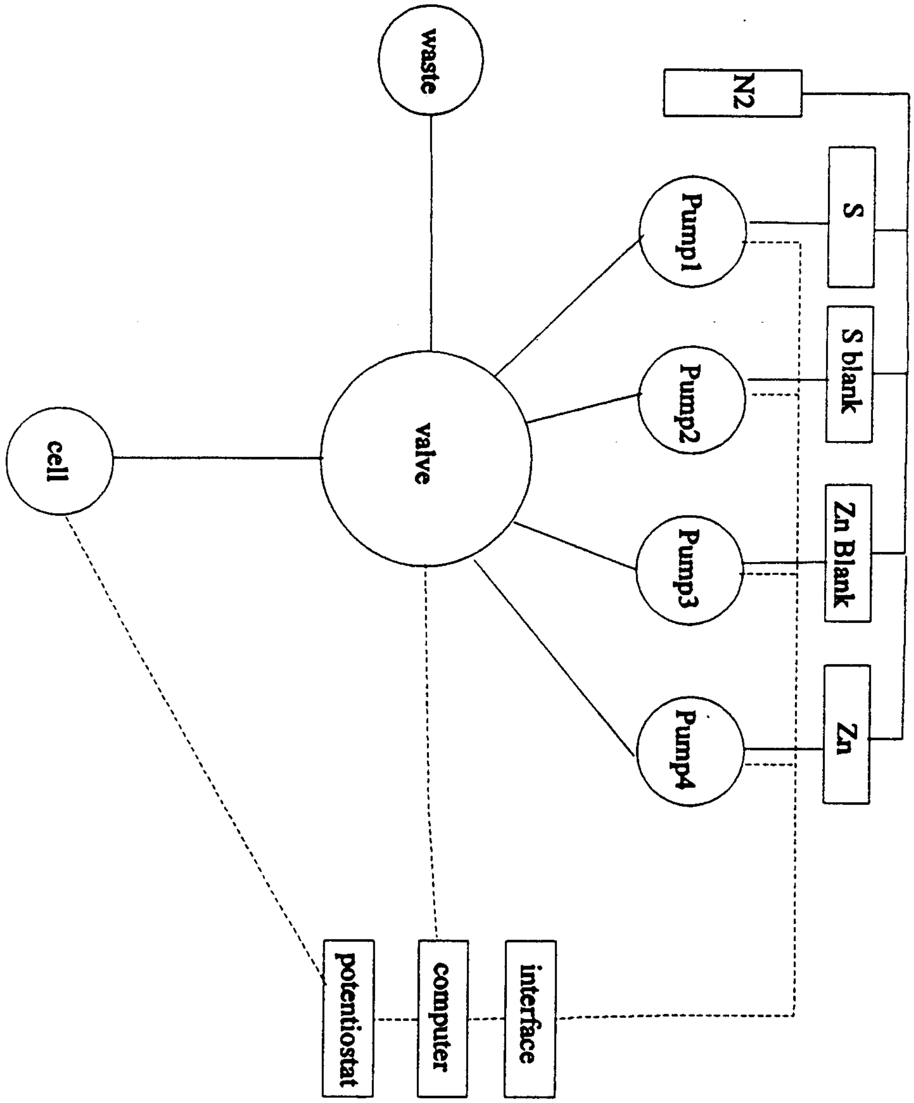
Figure 8: Glancing angle XRD of a film of 200 ZnS ECALE cycles .

Figure 9: SEM of a Ag doped ZnS film made with 200 ECALE cycles.

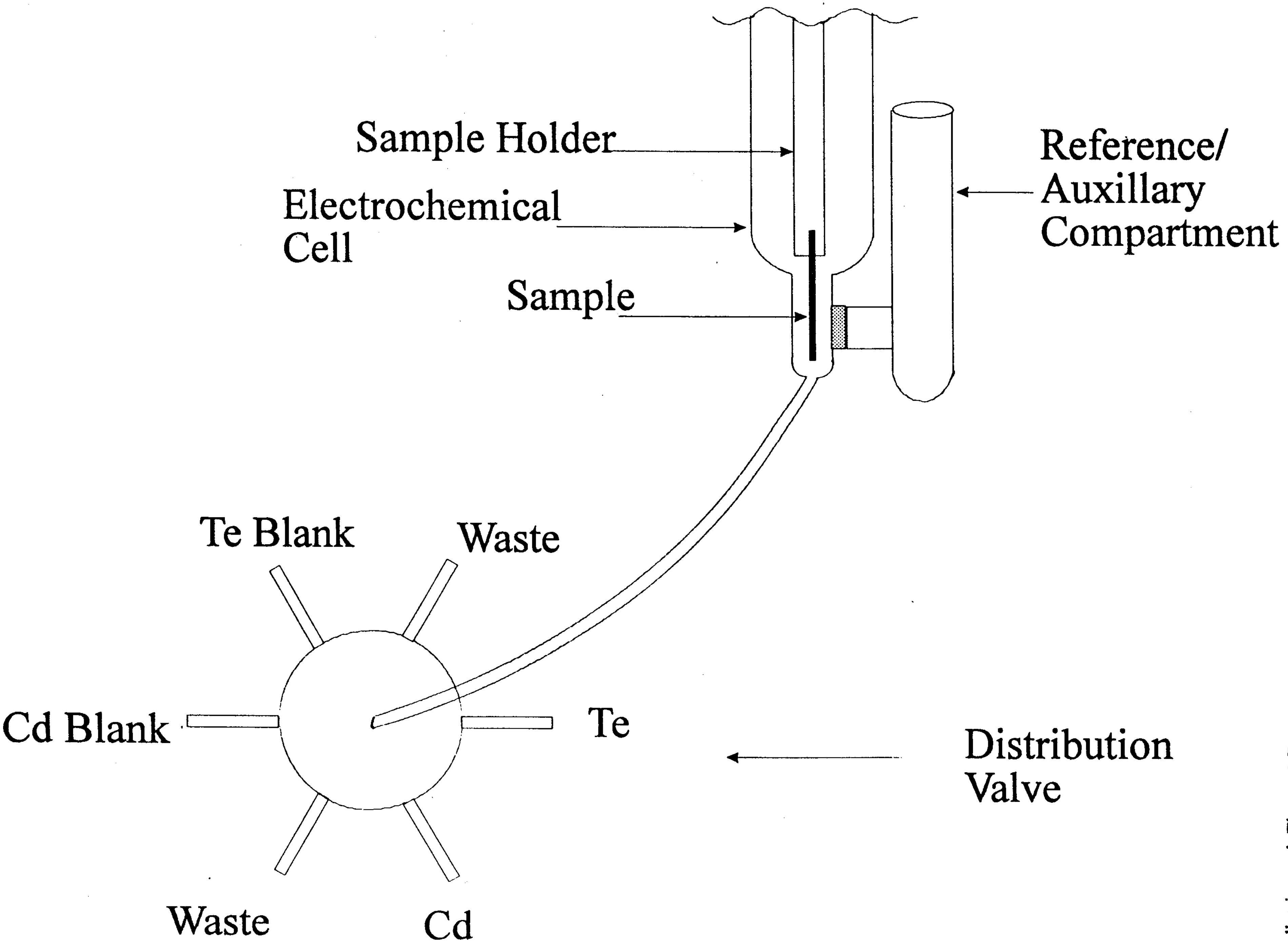
Figure 10: SEM of ZnS doped with Mn. A) At a magnification of 5700x F) At a magnification of 45600x.

Figure 11: Glancing angle XRD of doped ZnS films made with 200 ECALE cycles. A) Ag doped, B) Mn doped.

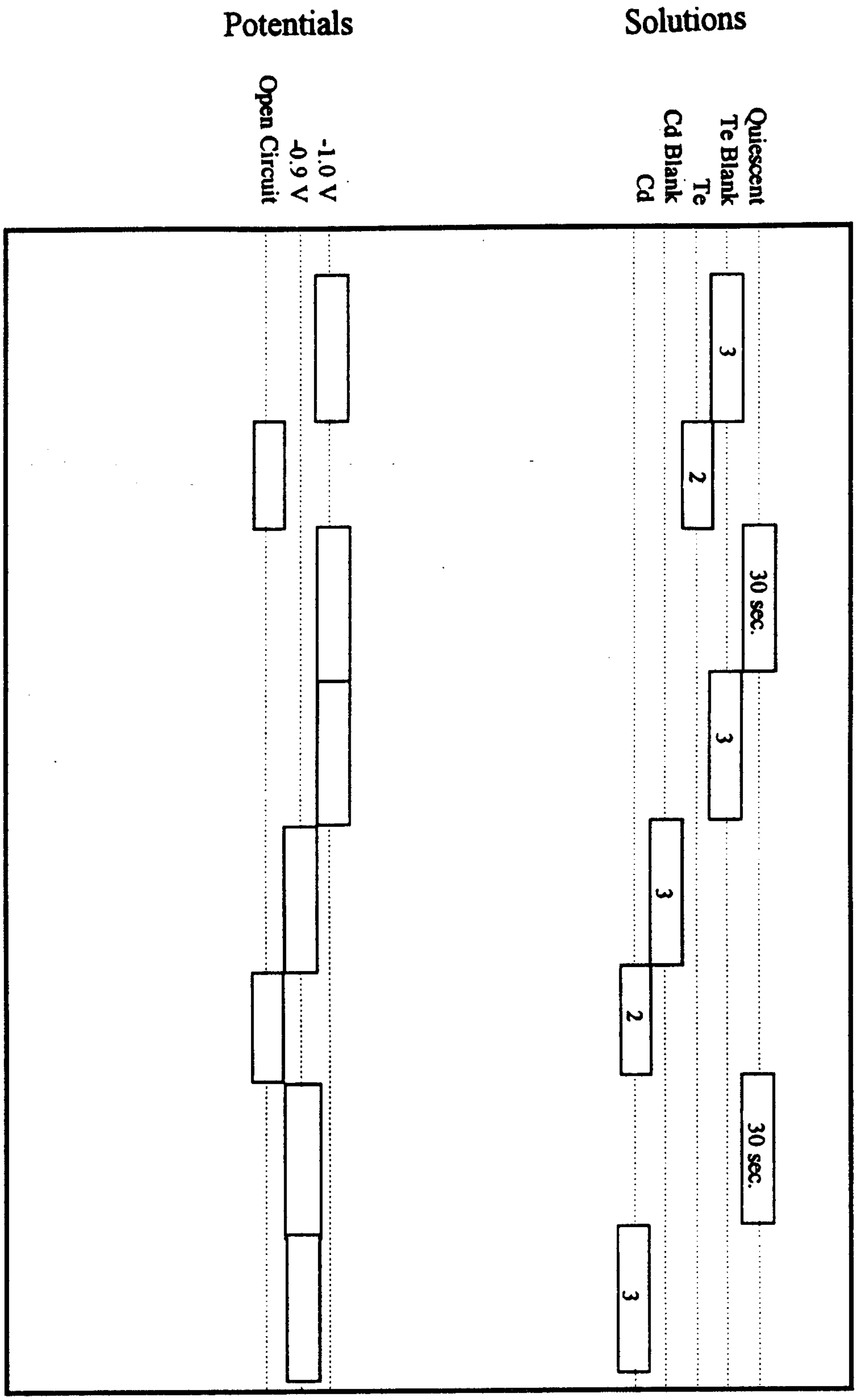
Figure 12: Cathodoluminescence of a Mn doped ZnS thin film on ITO. 200 ECALE cycles.



Colletti, et. al. Figure 1A



Colletti, et. al. Figure 1 B



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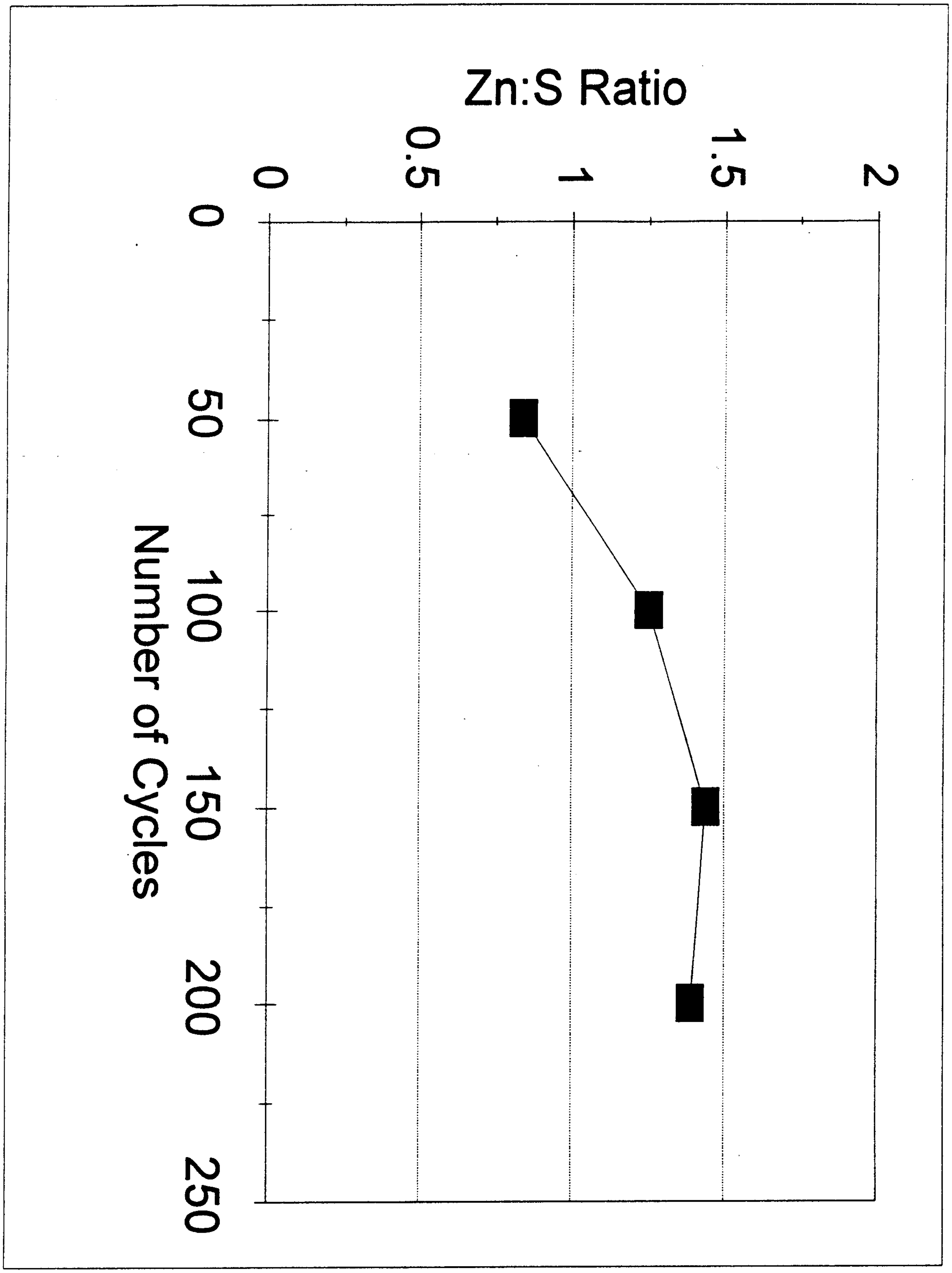

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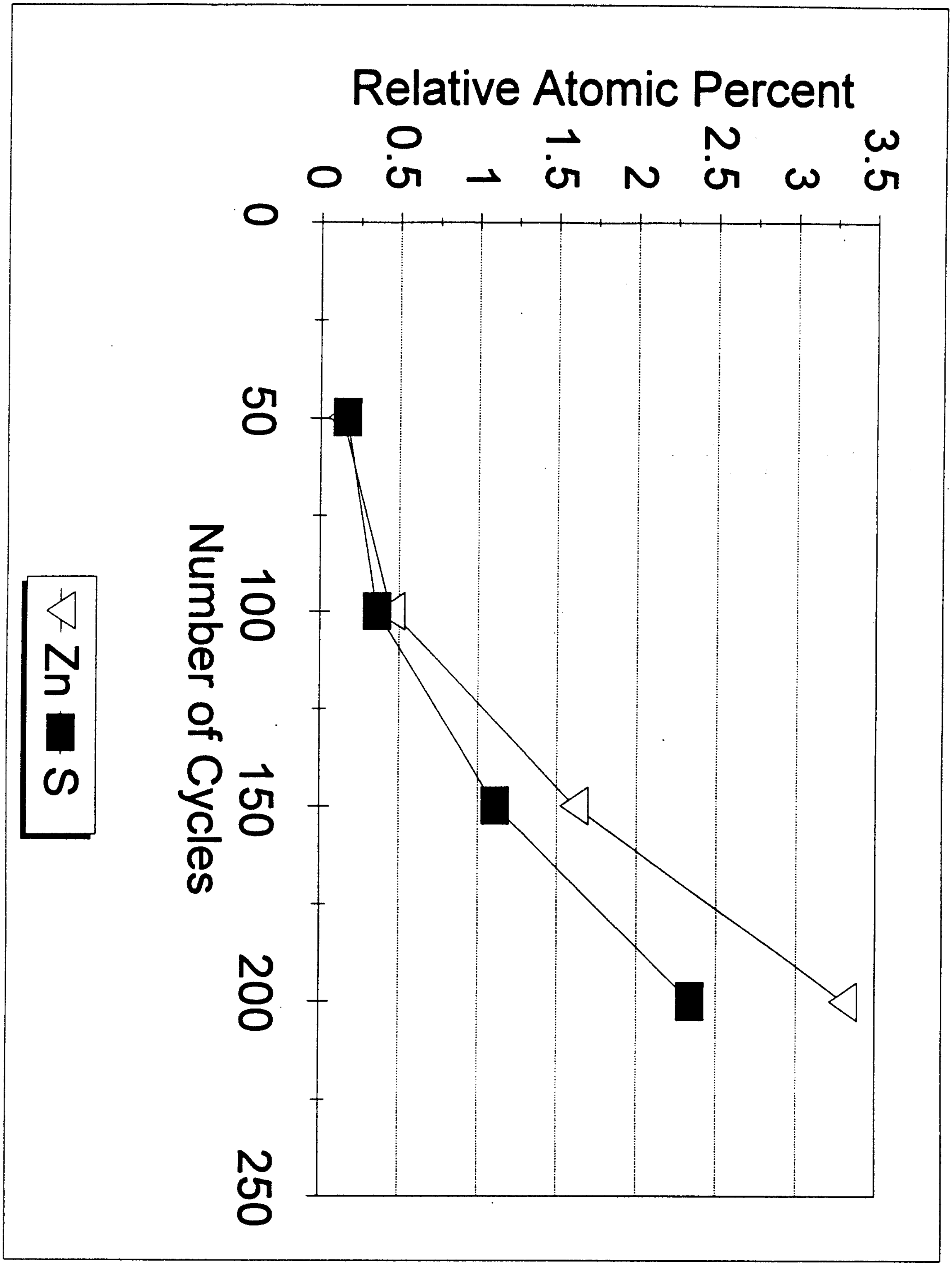

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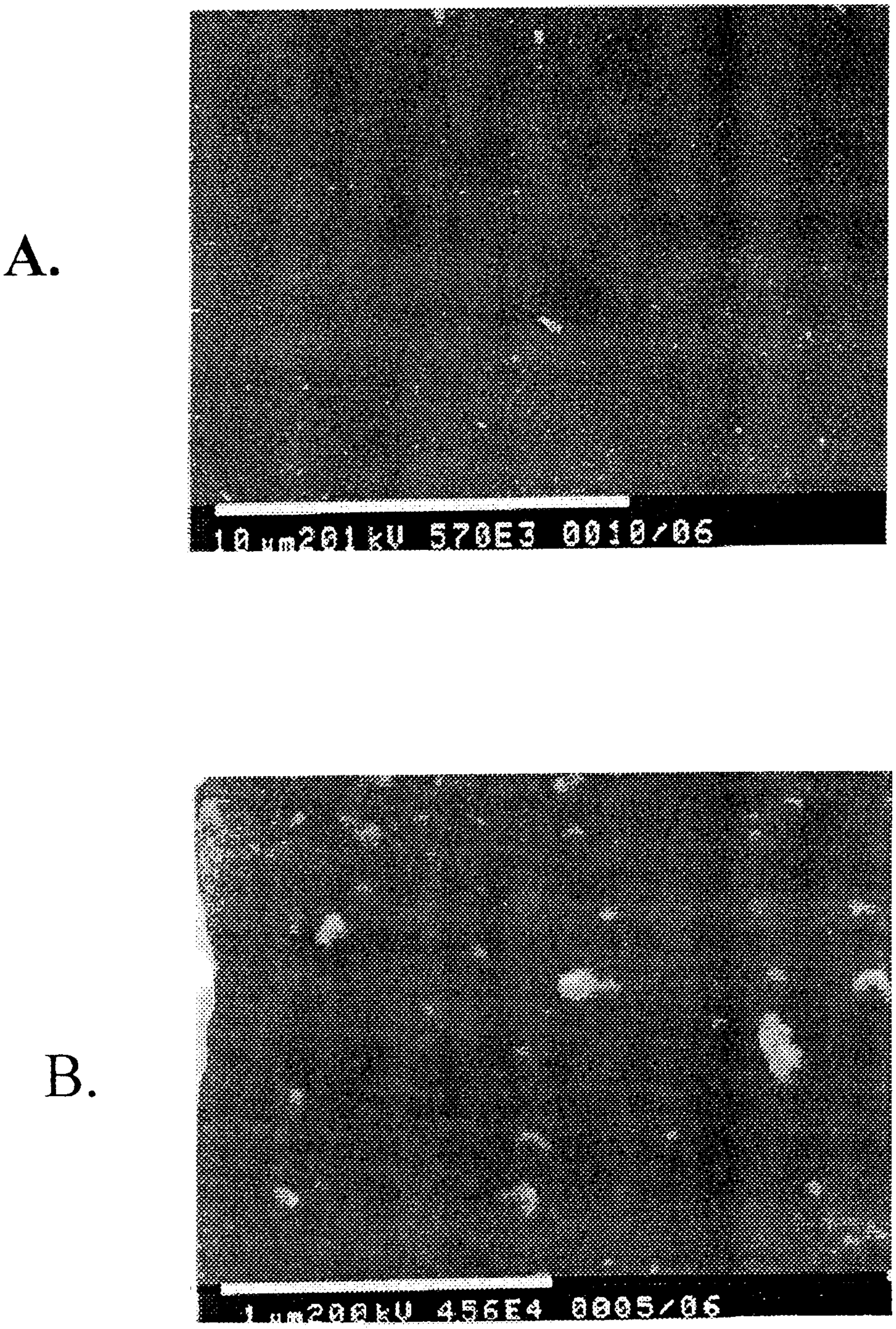
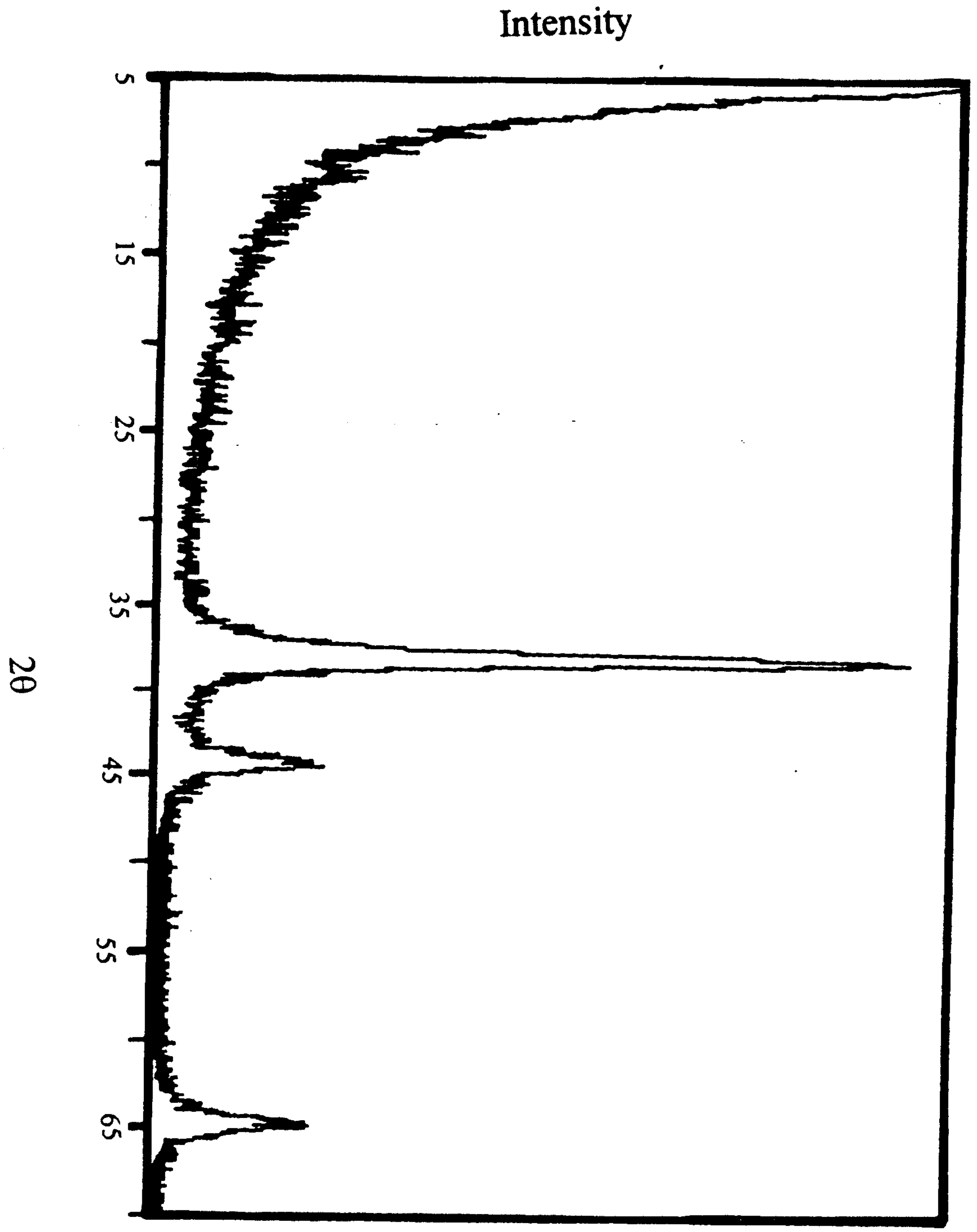


Colletti, et. al. Figure 5



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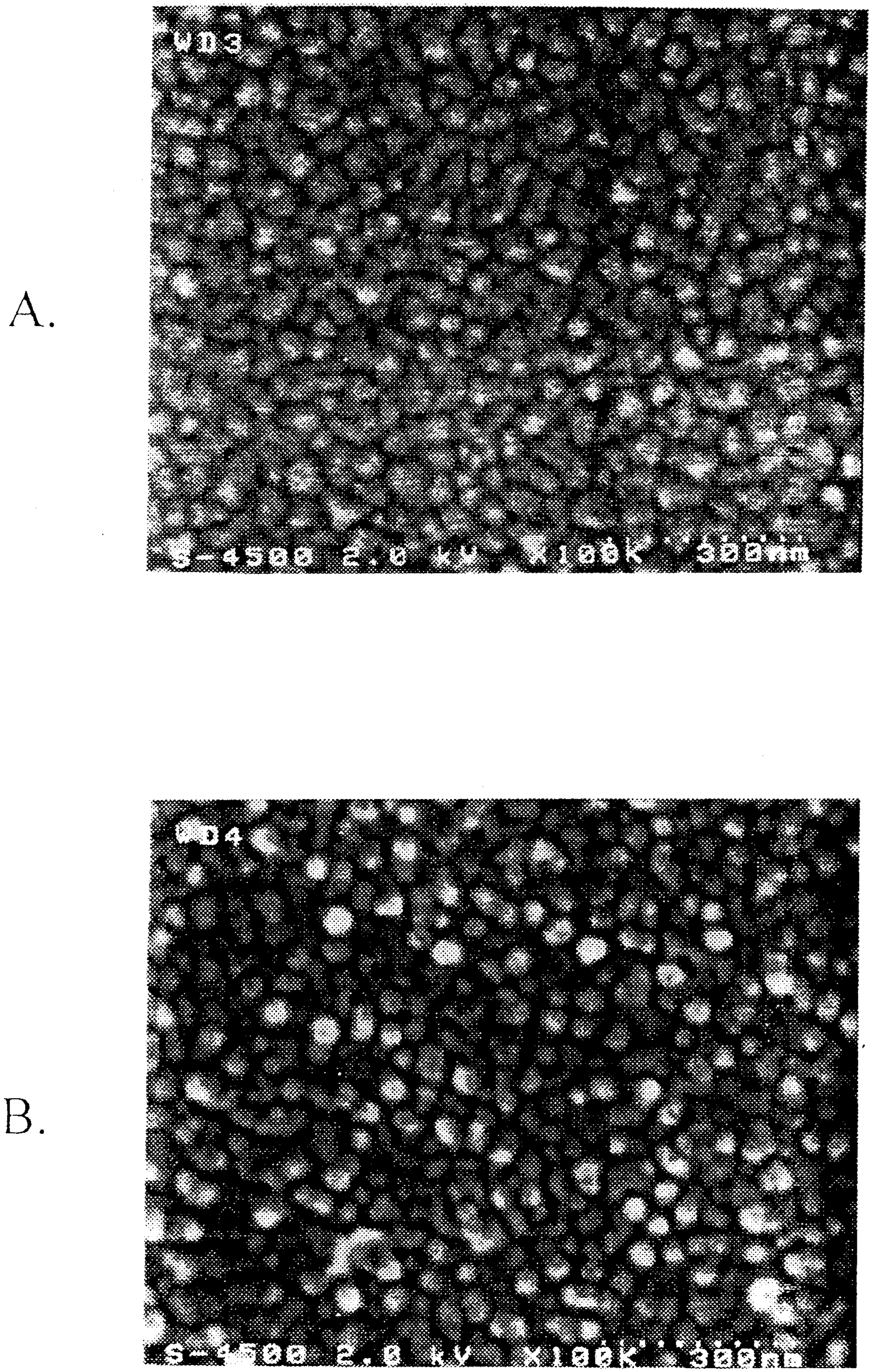
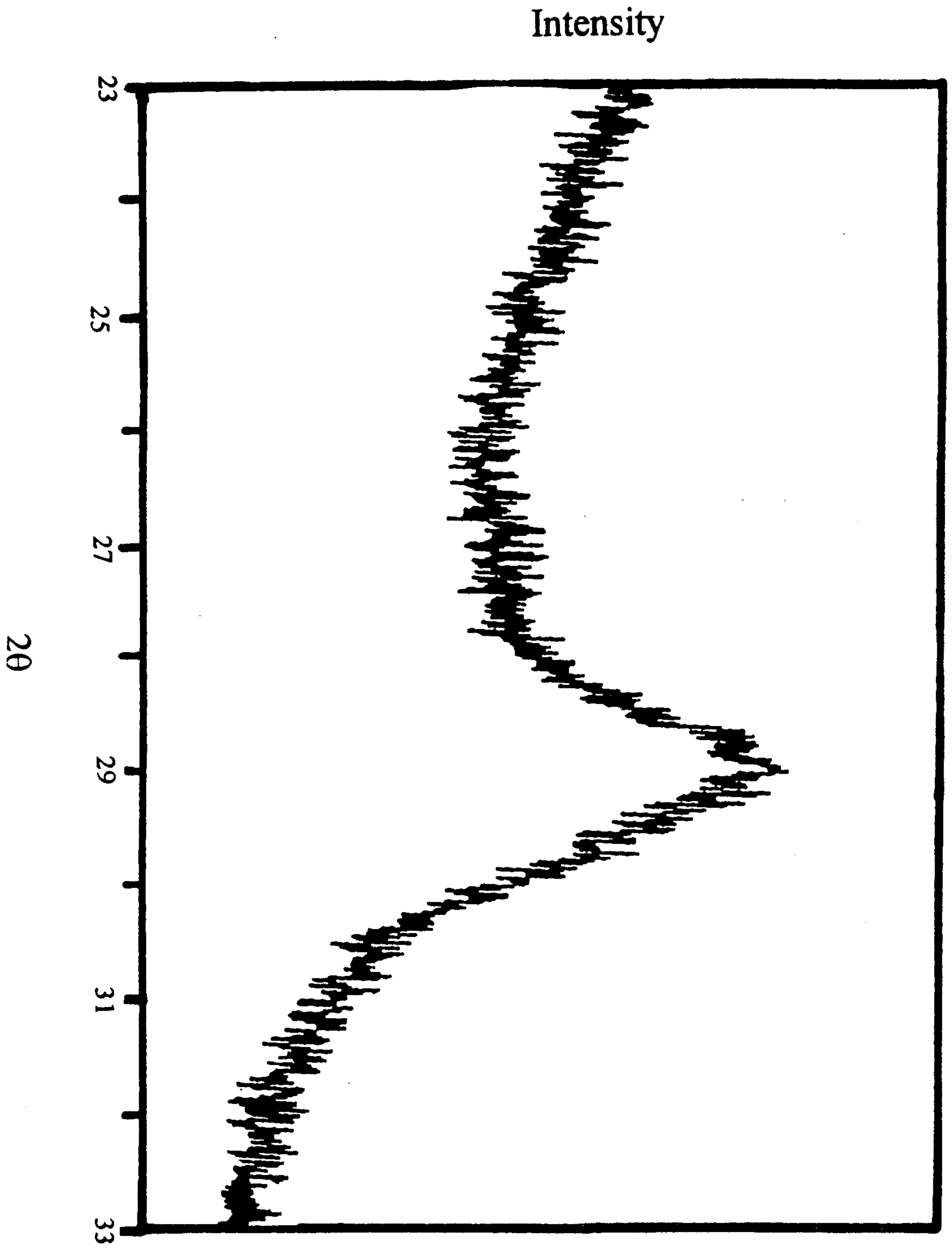


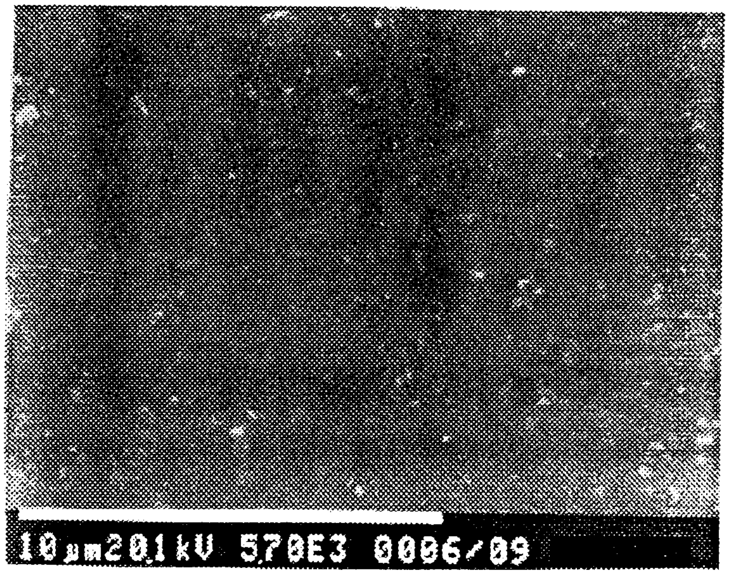
Colletti. et. al. Figure 7



Colletti, et al. Figure 8

Colletti, et. al. Figure 9

A.



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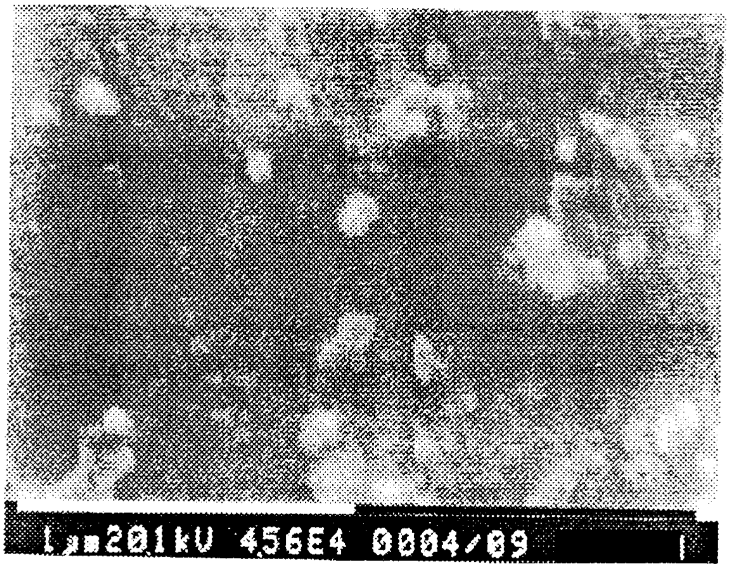
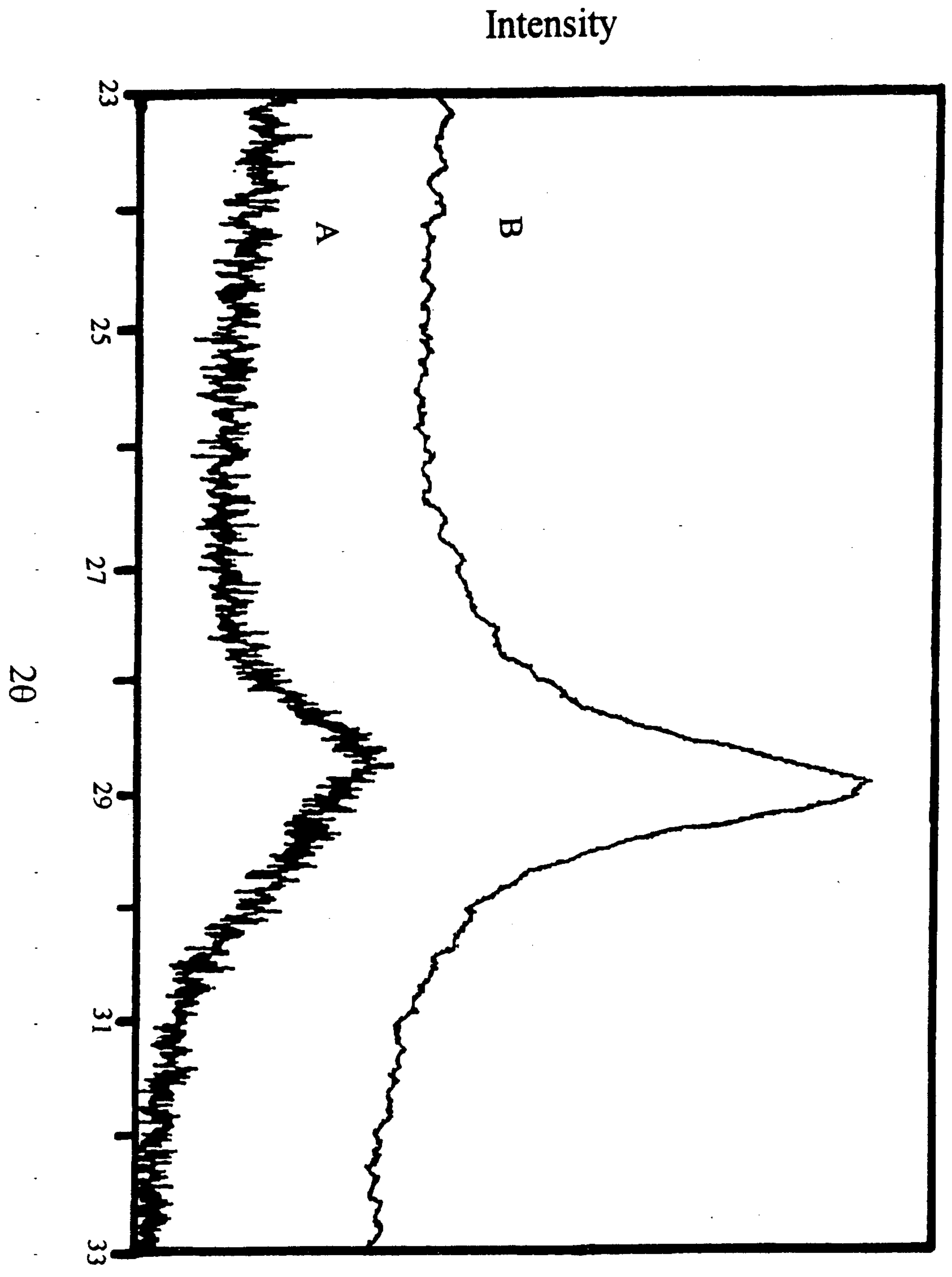
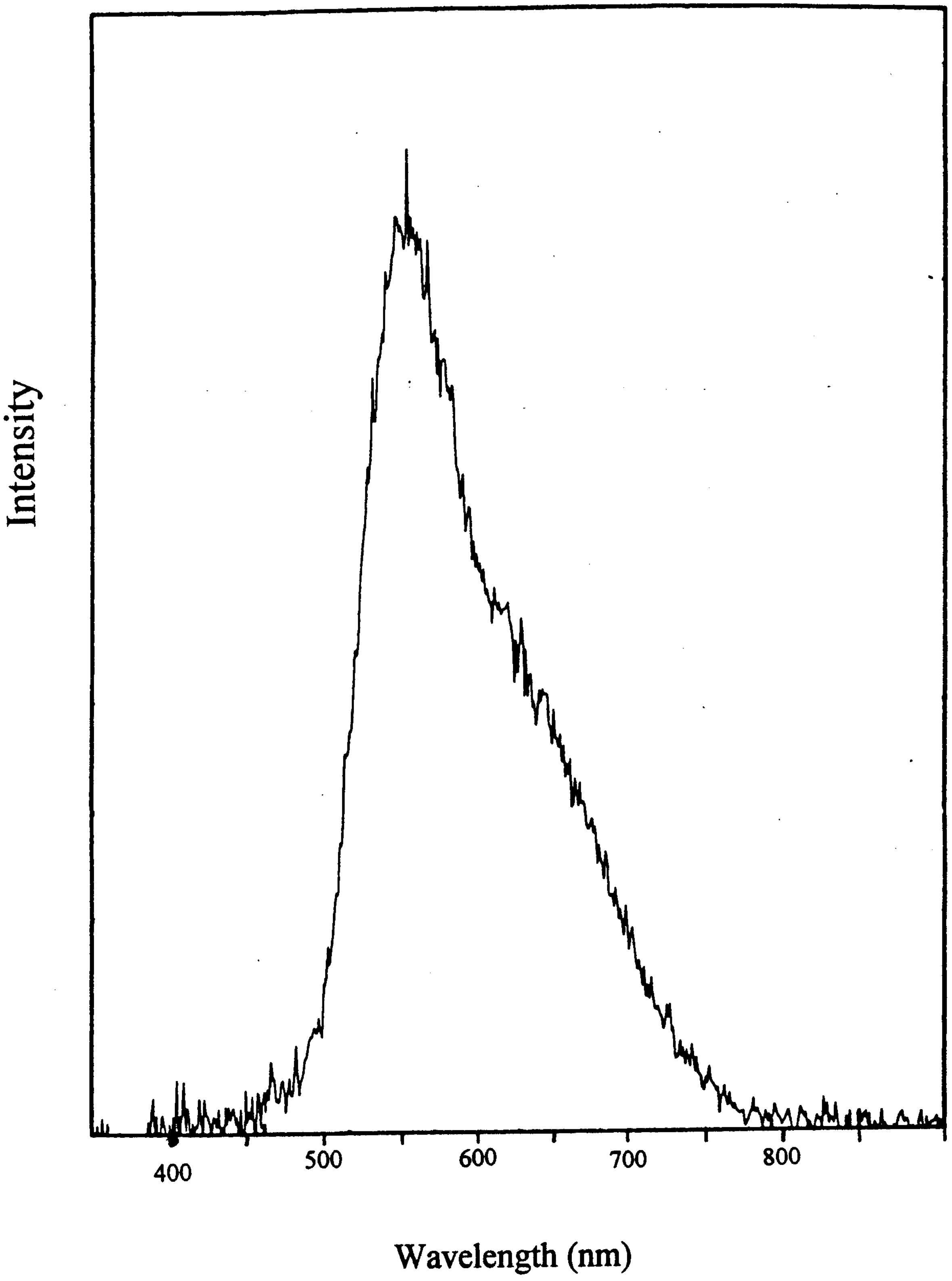


Colletti, et.al. Figure 10



Colletti, et al. Figure 11



Colletti, et al. Figure 12