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Final Technical Report
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SURFACE RAMAN SPECTROSCOPY FOR EVALUATION OF CONFORMAL WAFER LEVEL UNION ARCHITECTURES

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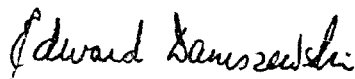
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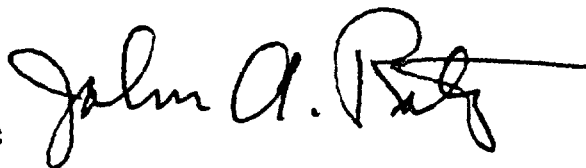
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Final Report for Expert Science-Task-A-9-1911 Order #18
by J. Chaiken

One goal was to produce ultrafine particles which could be used as precursors for interface fabrication. By coating metal oxide/ceramic particles with appropriate metals it was hoped to build up the lattice/matrix of an interface between a metal and metal oxide from a very small scale. On the smallest scale possible, we would be molecularly engineering the interface. We have succeeded in producing metal coated ceramics using laser induced chemical vapor deposition(LCVD). Specifically, we have good evidence supporting the claim that we can produce tungsten oxide films, i.e. tungsten bronzes(M_xWO_{3-x}) of varying stoichiometry(i.e. materials with varying x and M). The other goal was to implement a surface Raman spectrometer(sRs) which could be applied to the problem of characterizing model interfaces, i.e. in this specific Task metal coated ceramic particles, on the basis of the presence or absence of certain molecular structures. Manifested by the presence or absence of specific vibrational frequencies, evidence of structure on the molecular scale associated with a specific type of interfacial property can be identified and archived. We were able to produce clusters which were so small as to preclude obtaining Raman spectra of the non-associated particles/clusters. Other, non-Raman spectra, which do shed light on the nature of the material formed by the agglomeration of the clusters will be shown. We have succeeded in implementing a sRs apparatus which can also be used on the agglomerated materials and the process of collecting an appropriate data base is underway. In this Final Report we first present a section dealing with the fabrication of the metal-metal oxide ultrafine particles/materials. A second section describes the implementation of the Raman spectrometer. The final section will discuss some of the practical implications.

An interface between metallic materials and insulator/semiconductor type materials could be the site where most of the fundamental interactions occur that determine the properties of: 1) certain types of selected area heteroepitaxial structures of importance in IC fabrication and packaging, 2) advanced thermionic cathodes, 3) metal/ceramic electrical/cooling feedthroughs of vacuum electronic devices, and 4) metal-semiconductor/insulator structures related to other applications as well. Our first attempts to produce metal coated ceramics involved the direct interaction of alumina particles(Al_2O_3 , 10 μ average diameter) with organometallics species in the gas phase. Their interaction was to be driven/catalyzed by pulsed ultraviolet laser light. Using loosely focussed pulses not exceeding 10mJ total energy content and of 20 nsec duration, organometallic species are converted into free metal atoms/ions and a distribution of carbon containing neutral and ionic fragments by multiphoton dissociation(MPD). That this occurs is well established¹ to be the general case although the exact distribution of all species formed by MPD of a specific precursor has never been completely obtained. Our research involving intramolecular energy transfer² showed that certain propensities exist which might bear of the question of allowing control of the valence state of a metal atom which is being used to form a metal coated ceramic, but detailed information concerning the fate of the carbon/organic part of the organometallic precursor still remains elusive. Often, all these MPD products are incorporated into films which form from their coalescing on some nearby surface/substrate.

This was definitely the case with respect to LCVD onto the preformed alumina particles mentioned above. These particles would seem to have so much surface area that they collect the reaction products too well. Programmed reduction studies by the Schwarz group on alumina particles LCVD coated with chromium, using either chromium hexacarbonyl or benzene chromium tricarbonyl, quickly showed that there was much more organic material on the "as deposited metal coated particles" than there was reducible chromium. It might well be that subsequent heating in oxygen, at relatively low temperatures below what we would term

calcining temperatures, could be used to produce volatile carbon containing products which could be more easily driven from the particles. This is unlikely because for the particles treated with the hexacarbonyl, in which highly agglomerated carbonaceous materials would not seem to be major overall reaction products from either the MPD process or subsequent chemistry involving all the MPD products and the substrate, the same situation was observed. Note that surface Raman spectra by themselves do not absolutely establish the structure of a reaction product until suitable reference spectra can be obtained. For purposes of producing appropriate metal coated ceramic particles, we have established that the LCVD approach may still be viable, but either post-deposition treatments should be considered or the use of different precursors or substrates. It should be noted that the Raman spectrometer part of the Task requires that a spectrometer be assembled which is appropriate for assessing and evaluating the properties of the types of reference systems we are trying to form.

The latter option, essentially the use of a different substrate, proved to be successful for our current purposes but we note that for some applications like cathode formulation and production, post deposition treatments of 10 μ particles might be more appropriate. For selected area heteroepitaxy applications the choice of different substrate was more appropriate. In as much as the presence of carbonaceous impurities is an often observed characteristic of organometallic CVD produced materials using any kind of driving force, e.g. a laser or thermal chemistry, we were not surprised to find indications of the same using high surface area substrates. Since we desired to build up materials by interactions of metal coated ceramic particles, we considered the problem of forming both the ceramic particles and the metal coating simultaneously. This approach was suggested by our prior research³ on LCVD. We had already shown that it is possible to produce thin films of platinum with quite unusual optical and electrical properties. Very similar materials, prepared by researchers at AT&T labs⁴ using radically different means, apparently derived these same properties because of microstructure they argue is an artifact of the film formation process. They have direct evidence that their films are composed of clusters of metal atoms, and all our observations, including Scanning Electron Micrographs (SEM) obtained at RB directorate instrument by Lt. B. Vastag, support the idea that we can produce similar microstructures using LCVD.

Platinum is exceedingly resistant to oxidation so it seemed that use of comparable reaction conditions as for production of platinum films, but involving a metal having a richer oxide chemistry, would allow formation of ceramic particles by oxidation of metal atom clusters *as they are formed*. The metal oxide clusters/ceramic particles would then be coated by more metal atoms, as the oxide clusters are formed, thus finally producing the desired metal coated ceramic particles. Affecting this sequence of events would be the consequence of carefully choosing the relative concentrations of gas phase organometallic and molecular oxygen, flow rate, temperature of substrate and gas phase, presence and nature of added buffer gas and other factors as well. From conventional bulk metal-oxygen chemistry, it is to be expected that the oxidation step will be highly exothermic thereby increasing the fragmentation rate and affecting the distribution of cluster sizes produced. We emphasize that both inter and intramolecular energy transfer considerations will be important in attaining a predictive understanding of the process. In the end it was hoped that a material could be formed which would be demonstrably nonstoichiometric by independent means, but amenable to sRs for purposes of demonstrating that the instrument works. All these goals were achieved, thus successfully completing the Task, but many questions relating to the characteristics of the sRs apparatus and the materials produced still remain.

Tungsten bronzes are well known⁵ materials although, to our knowledge, they have never been produced in thin film form or by methods compatible with semiconductor device fabrication. The lack of genuine samples which could serve as references for spectroscopic studies precludes our being able to unambiguously assign sRs spectral features. In addition, we

are in the process of trying to obtain x-ray diffraction measurements from samples scraped off of substrates. Unit cell dimensions and possible evidence relating to predominant morphologies of the crystals which would be useful in predicting possible space groups for complete vibrational assignments are needed. Other types of independent measurements have provided our strongest evidence so far. Auger data, as in Figure 1, has conclusively shown that we can produce tungsten-oxygen films of widely varying stoichiometry. This particular Figure suggests a stoichiometry of roughly W_{50} independent of depth which, at the deepest, could not have been less than a few monolayers. Note that this stoichiometry was still largely intact after prolonged contact with air but within a few tens of seconds of starting heating in air with a heat lamp to no higher than 340 K, the resistivity becomes larger quickly, in a nearly discontinuous fashion. The heating presumably promotes reaction of the film with oxygen and this possibility is being investigated further. For this same film, and of course a number of others which are not displayed here, resistivity and temperature coefficient of resistivity were measured and one set of measurements are shown in Figure 2. The resistivity is clearly much greater than for bulk tungsten and increases roughly exponentially with temperature suggesting in both cases that the film is a semiconductor as is already known for bulk tungsten bronzes. We have shown that the color of the films, due to a significant reflective loss in the visible as is also known for the bulk tungsten bronzes, is clearly a function of the relative proportions of gas phase oxygen and organometallic precursor at the instant the laser pulse is present. A UV-visible transmission loss spectrum of this same film before heating in air is shown in Figure 3 and it should be remembered that the apparent absorption indicated near ≈ 600 nm actually corresponds to a reflective loss. Given the optical and electrical properties of these materials, they would certainly seem to match the known properties of tungsten bronzes well and we conclude for now that that is what we have indeed made. As a final note added in proof, we have recently become aware of work being carried out in the Soviet Union⁶ and being submitted for publication in the American scientific literature which recounts the production of metal clusters by exactly the process we have employed. Their work relied mostly on optical emission from the laser produced 'cloud' and Rayleigh light scattering by that cloud and we find their experience with LCVD molybdenum to be quite similar to our own with tungsten.

The Raman spectrometer is represented in Figure 4. It consists of three main subsystems. The vacuum chamber with sample manipulation capability is one system. The laser and associated light collection optics for introducing the excitation light into the vacuum chamber and collecting the Raman scattered light is a second system. The spectrograph/optical multichannel analyzer(OMA) combination which together disperse and record the spectrum of the collected Raman scattered light comprise the third main subsystem. While requiring considerable care and diligence to obtain high quality spectra, we do believe that the technology of surface Raman spectroscopy is sufficiently well documented elsewhere⁷ as to obviate a detailed discussion of all but the unusual features and more salient capabilities of our system. It should be noted that while we have successfully completed the assigned Task, there is still considerable experience to be gained with an apparatus as intricate and complex as our sRs. In addition, we note again that the types of materials we have made would seem to have no simple alternative synthesis apparently precluding our obtaining spectra of reference compounds. Having reference spectra of other materials besides stoichiometric WO_3 , and W after exposure to air would allow a reasonable chance of assigning the spectra we have observed so far. All our results, including sRs spectra when all reference spectra are obtained, will be published in either the Journal of the American Chemical Society or the Journal of Physical Chemistry. What we are reporting here is that we have synthesized thin films of nonstoichiometric tungsten oxides by a unique photochemical/physical mechanism involving ultrafine particles/clusters and that we have assembled the components for a sRs and they function satisfactorily. The sRs spectra which have been obtained so far are either, routine standards such as would be commonly employed for calibration purposes e.g. WO_3 , or those taken from LCVD produced materials which have no easily accessible bulk counterpart. When a detailed analysis of these

spectra of unknown materials is as complete as we can accomplish, and we have not yet given up trying to access bulk reference compounds, the results, including sRs spectra, will be published.

For all practical purposes we have succeeded completely. We have assembled a sRs with ≈ 10 micron spatial resolution, which can be used on a wide variety of samples in high/ultra high vacuum. High temperatures limited by the survivability of the samples and the accompanying black body radiation background are accessible. The system is particularly well suited to in-situ probing of thin films formed by LCVD. Raman shifts as small as ± 350 cm⁻¹ from the Rayleigh line can be detected with very little background. Spectra can be obtained from solid samples in under an hour of collection time with only a few tens of milliwatts of incident excitation. The dye laser portion of the system, which is not yet fully operational, will permit excitation profiles to be measured thus giving important electronic structure related information. During the course of the Task, two Graduate Research Assistants, Mike Casey and Martin Villarica, both U.S. citizens, contributed substantially while they received considerable training in sRs and LCVD technology. We must also acknowledge the assistance of Dr. L. Walsh, and Mr. Ibars Irbe of the RB directorate for invaluable assistance in characterizing some of our materials. We are pleased that we have accomplished so much within a single year despite the fact that our laboratories were relocated during the funded period which diverted our time and effort substantially. The results obtained so far support a strong expectation that continued effort will provide useful information relating to critical applied areas such as understanding the properties of certain types of selected area heteroepitaxial structures of importance in IC fabrication and packaging, the operation of advanced thermionic cathodes, and the failure chemistry associated with metal/ceramic electrical/cooling feedthroughs of vacuum electronic and other devices. Indeed, we speculate that the most useful sRs reference spectra we will ultimately obtain will come from samples of selected area heterostructures of practical interest associated with operating and failed semiconductor devices, real thermionic cathodes at various stages of their lifetimes, and surfaces of metal-ceramic feedthroughs which have failed in service.

¹ for purely gas phase processes see A. Gedanken, M. B. Robin, and N. A. Kuebler, J. Phys. Chem. 86, 4096(1982), in the context of film deposition see N. S. Gluck, G. J. Wolga, C. E. Bartosch, W. Ho, and Z. Ying, J. Appl. Phys. 61, 998-1005(1987)

² See B. Samoriski and J. Chaiken, J. Chem. Phys. 90, 4079-4090(1989) and references therein.

³ D. Rooney, D. Negrotti, T. Byassee, D. J. Macero, B. Vastag, J. Chaiken, accepted J. Electrochemical Soc. accepted 10/26/89

⁴ See J. D. Porter, A. Heller, D. E. Aspnes, Nature 313, pp. 664-666(1985) and references therein. Later references are also available.

⁵ See Cotton and Wilkinson in "Advanced Inorganic Chemistry" third edition(1972), page 948. see also P. G. Dickens and M. S. Whittingham, Quart. Rev. 22,30(1968)

⁶ A. V. Dem'yanenko, A. A. Puretzky, submitted J. Phys. Chem. 5/25/1989

⁷ see for example R.G Greenler and T.L.Slager, Spectrochim. Acta, 29A,193(1973) or M. Fleischmann, P. J. Hendra and A. J. McQuillan, Chem. Phys. Lett. 26, 163(1974) or Y. J. Chen, W. P. Chen, and E. Burstein, Phys. Rev. Lett. 36,1207(1976) or for an exhaustive review complete through 1979 see R. P. Van Duyne in "Chemical and Biological Applications of Lasers", edited by C. B. Moore(Academic Press, 1979)

Figure 1

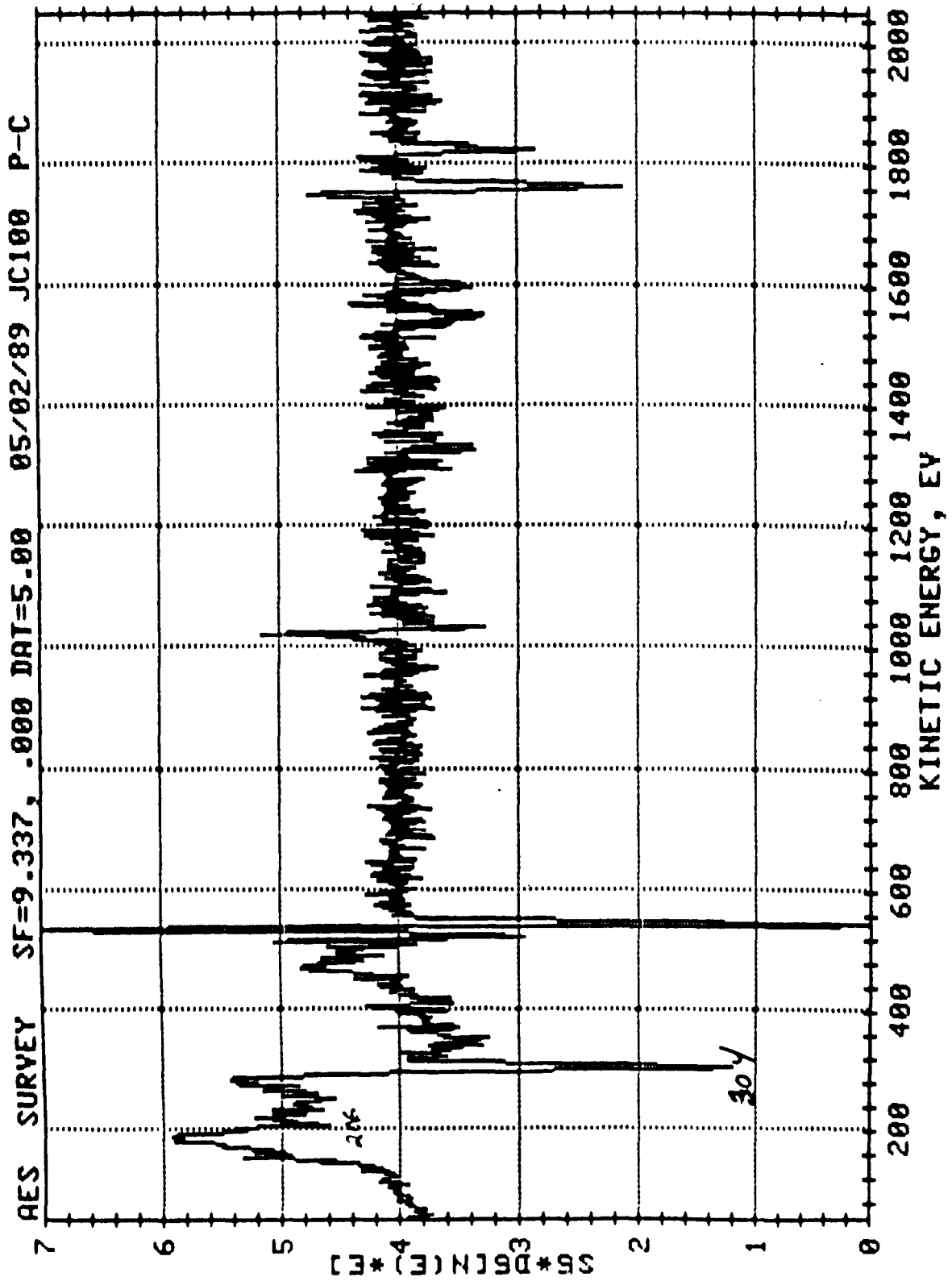


Figure 2

temperature dependence of laser deposited tungsten oxide resistivity

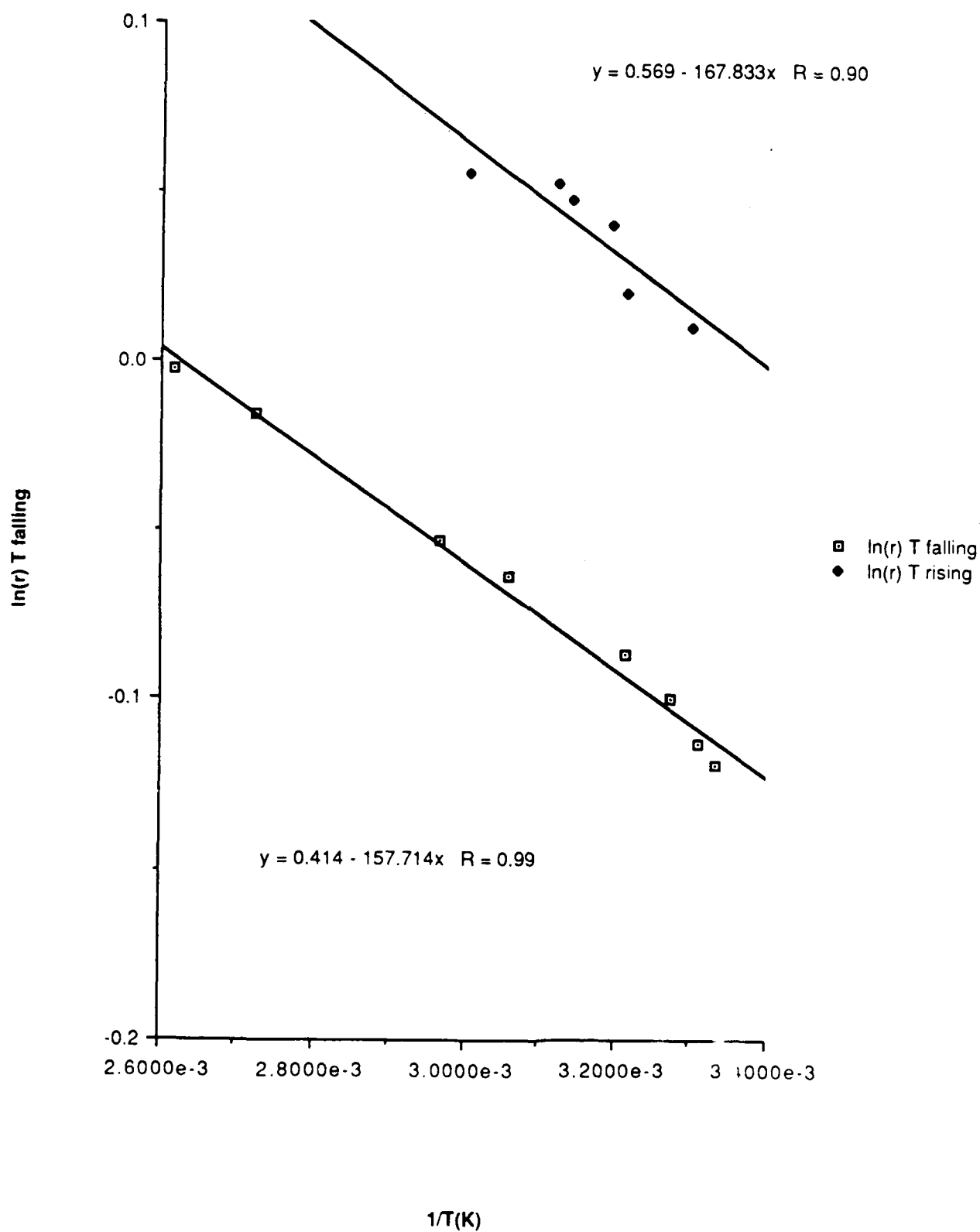
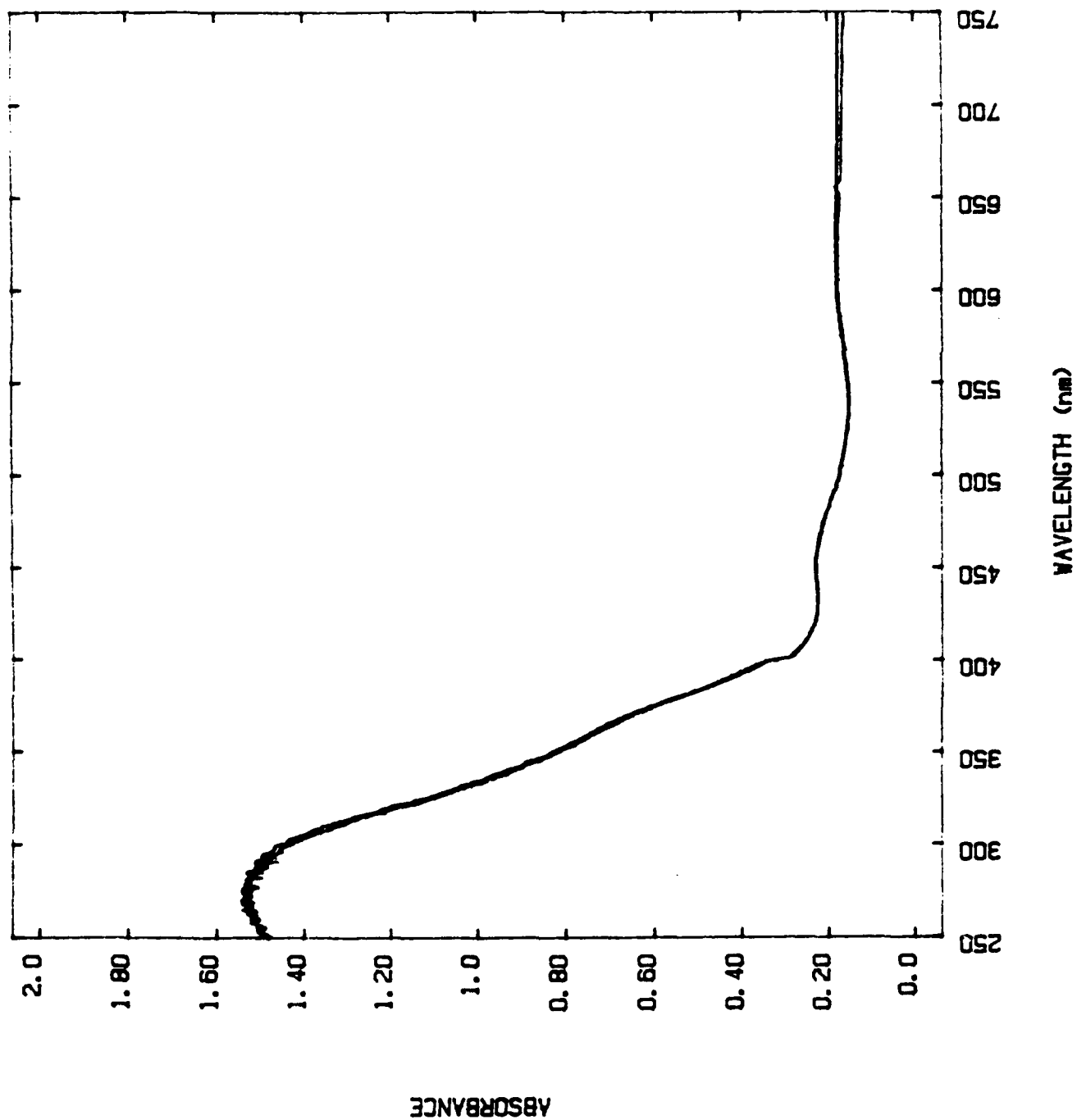


Figure 3

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Surface Raman Apparatus

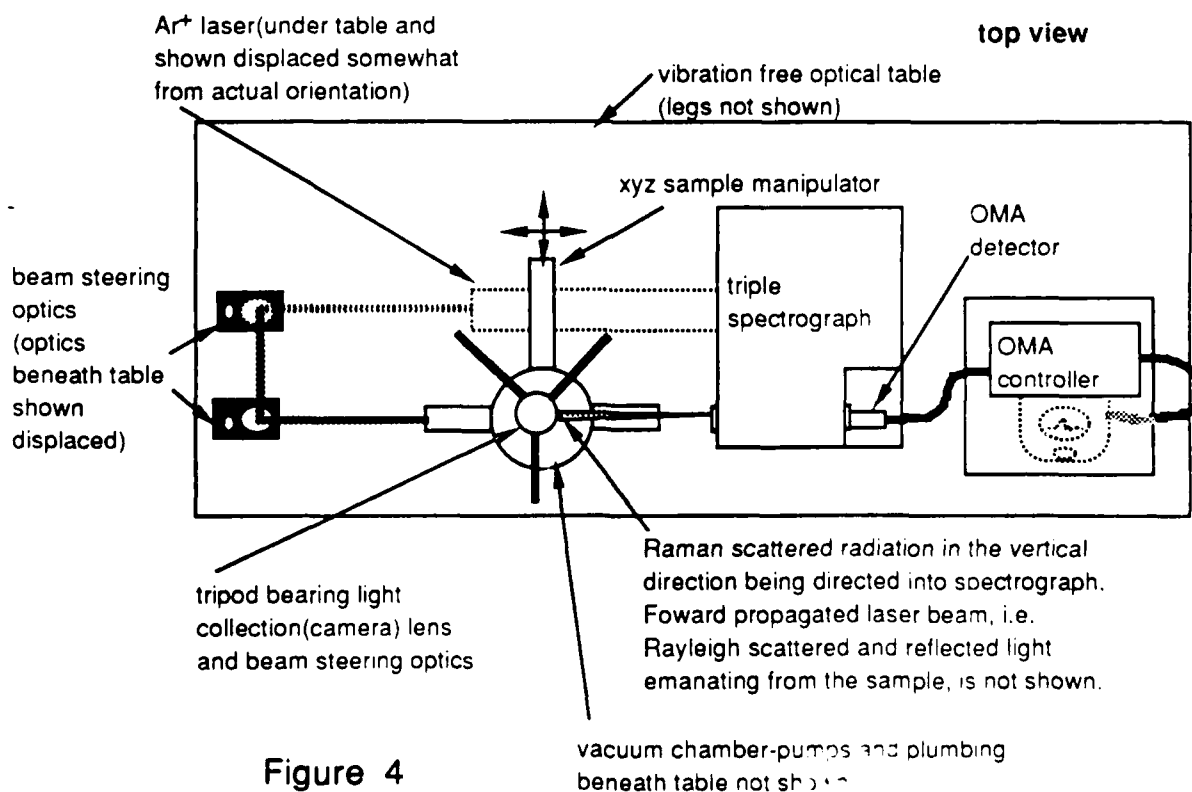
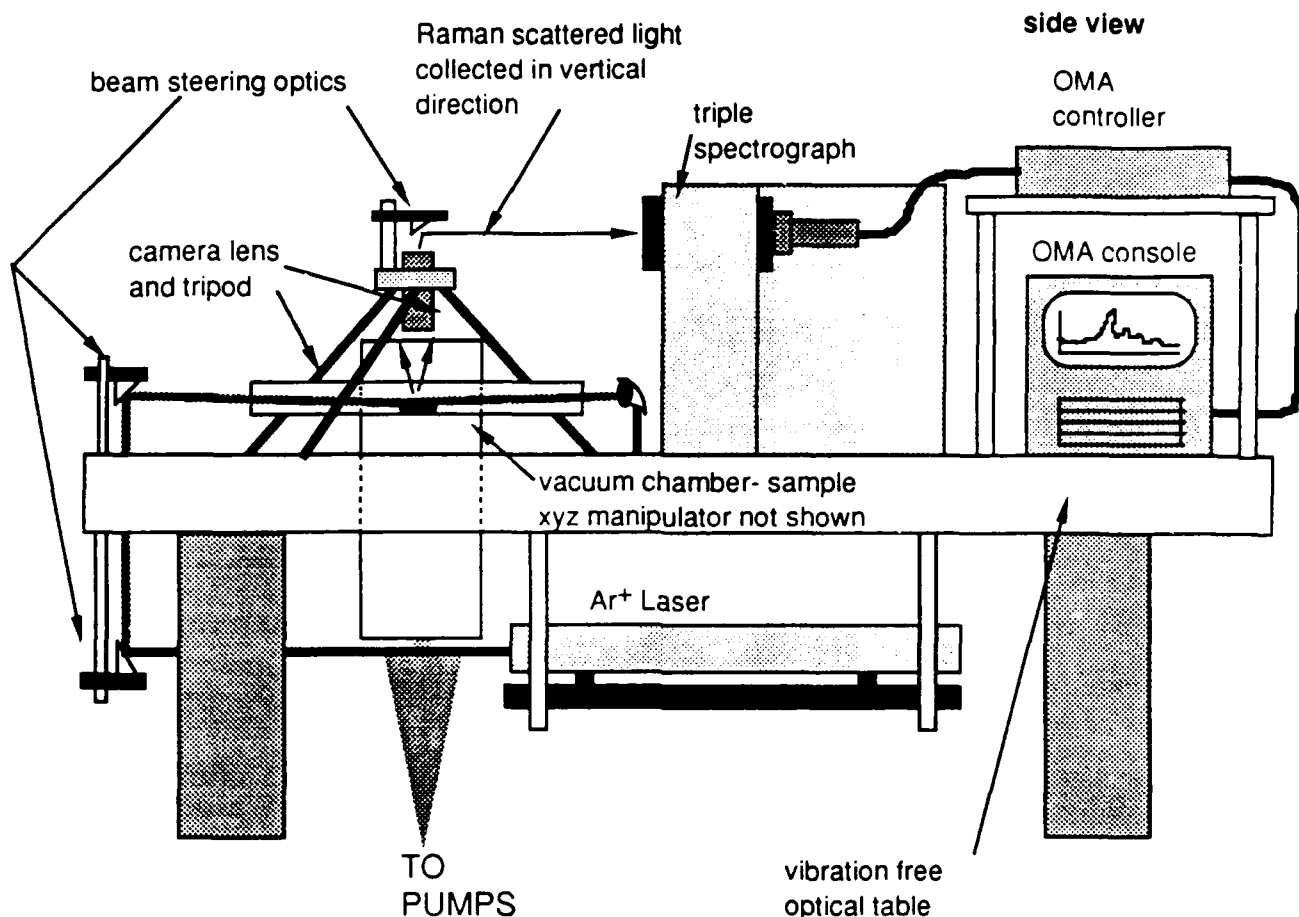


Figure 4