

Passivity Breakdown on Solid Versus Liquid Gallium

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ABSTRACT

Pits are found to nucleate on solid gallium in buffered chloride solutions, and we propose that the pits nucleate from blisters that form beneath the passive film on the metal substrate. The proposed association of pitting with blister formation is accounted for by the point defect model for the growth and breakdown of passive films, and has been tested by comparing the behaviors of solid and liquid gallium upon anodic polarization in chloride-containing environments. This study shows that liquid gallium resists passivity breakdown much more readily than does the solid, which we attribute to the inhibition of cation vacancy condensation, in liquid substrate, and hence to the formation of blister precursors at the metal/film interface. Thus, solid gallium is added to the growing list of metals and alloys that apparently suffer passivity breakdown via a vacancy condensate precursor.

The passive films on the surfaces of metals and alloys allow structurally important materials, notably aluminum alloys, iron alloys, and stainless steels, to be the basis of our metals-based civilization. Were it not for the protective nature of these films, the underlying metals quickly revert back to the oxidized states from which they were recovered, thus severely shortening the useful lifetimes of components made from these materials. An enormous amount of energy is added to these materials to elevate them to a state in which their properties meet design criteria, and it is the passive film that maintains the substrate in this high energy state. Hence, it is the phenomenon of passivity breakdown that defines the initial step in the deterioration of most structural materials, and any attempt to describe the kinetics of degradation of metals and alloys must necessarily address the phenomenon of passivity breakdown.

The point defect model (PDM) for the growth and breakdown of passive films on metals and alloys,¹⁻⁵ proposes that pitting corrosion is initiated via the condensation of cation vacancies at the metal/film interface, or possibly by destruction of the film at the film/solution interface via vacancy-pair coalescence. As argued elsewhere,^{2,4} conditions may exist, particularly in the presence of an aggressive anion in an aqueous environment, that increase the flux of cation vacancies across the film. If the vacancies arriving at the metal/film interface cannot be annihilated by the oxidative injection of cations from the metal, the vacancies may coalesce resulting in the local decohesion of the barrier layer from the metal substrate. Vacancy coalescence or condensation at the inner interface of an oxide scale is a well-documented phenomenon in the high temperature oxidation of metals exposed, generally, to air or oxygen.⁶ Here, we consider the two mechanisms for vacancy condensation at the metal/film interface as the precursor events in the breakdown of the passive films solid and liquid Ga in deaerated borate-buffer + KCl solutions. We contend that the experimental findings are in agreement with those predicted by the PDM, in that solid Ga exhibits blistering beneath the passive film as the precursor to the formation of pits. For low chloride concentrations, the liquid phase does not exhibit breakdown over the same voltage range, which we attribute to the fact that the liquid phase does not readily allow vacancy condensates to form. (Voids may form in liquids under cavitation conditions and if the rate of injection of vacancies is sufficiently high.) At higher [Cl⁻], liquid Ga does experience localized passivity breakdown in the form of dissolution/precipitation phenomena, but the morphology of the attack is fundamentally different than that observed on the solid. In this article we report preliminary data on passivity breakdown on solid *vs.* liquid gallium in buffered chloride-containing solutions. Full experimental details and a comprehensive discussion of the results will be presented at a later date.

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The PDM and Passivity Breakdown

The mechanisms for passivity breakdown, as provided for by the PDM^{2,4} are diagrammed in Fig. 1. Enhanced cation vacancy flux in the barrier layer may be caused by the absorption of an aggressive anion into a surface oxygen vacancy. Typically, chloride ion is the responsible anion, since it is prevalent in many environments, and because the combination of ion size and Gibbs energy of dehydration favors the absorption of chloride ion, compared with other anions, into surface oxygen vacancies on many metals.^{4,7} In one mechanism (case I, Fig. 1), the loss of oxygen vacancies at the film/solution interface is compensated for by a Mott-Schottky pair reaction, which also generates cation vacancies. This reaction is autocatalytic since oxygen vacancies are replenished, and hence may react with other anions in solution. Desorption of the anion along with a neighboring surface cation also may occur to generate an anion vacancy/cation vacancy pair at the surface and a metal cation and the anion in solution (case II, Fig. 1). If the cation vacancy diffusivity in the film is high, the cation vacancy of the vacancy pair may submerge into the film leaving the oxygen vacancy to react with another halide ion, which makes this process autocatalytic as well. As noted above, if the additional cation vacancies created by these mechanisms are not annihilated at the metal/film interface, and

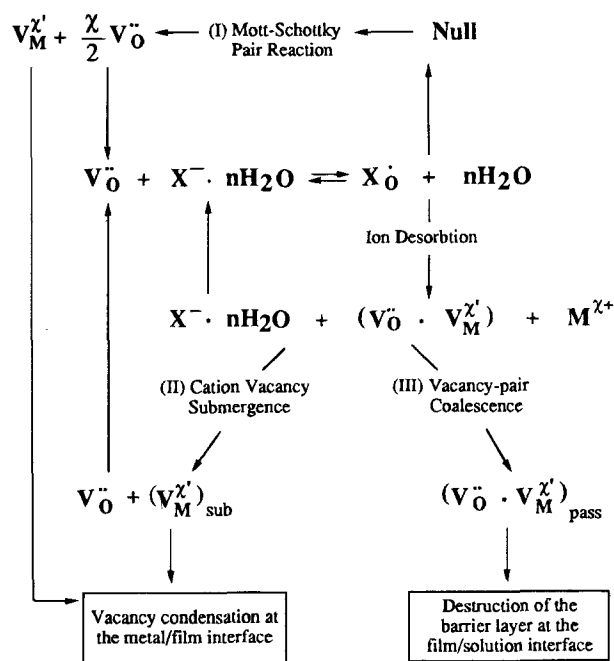


Fig. 1. Proposed mechanisms for passivity breakdown according to the point defect model are cation vacancy condensation at the metal/film interface (case I and II), and vacancy pair coalescence at the film/solution interface (case III).

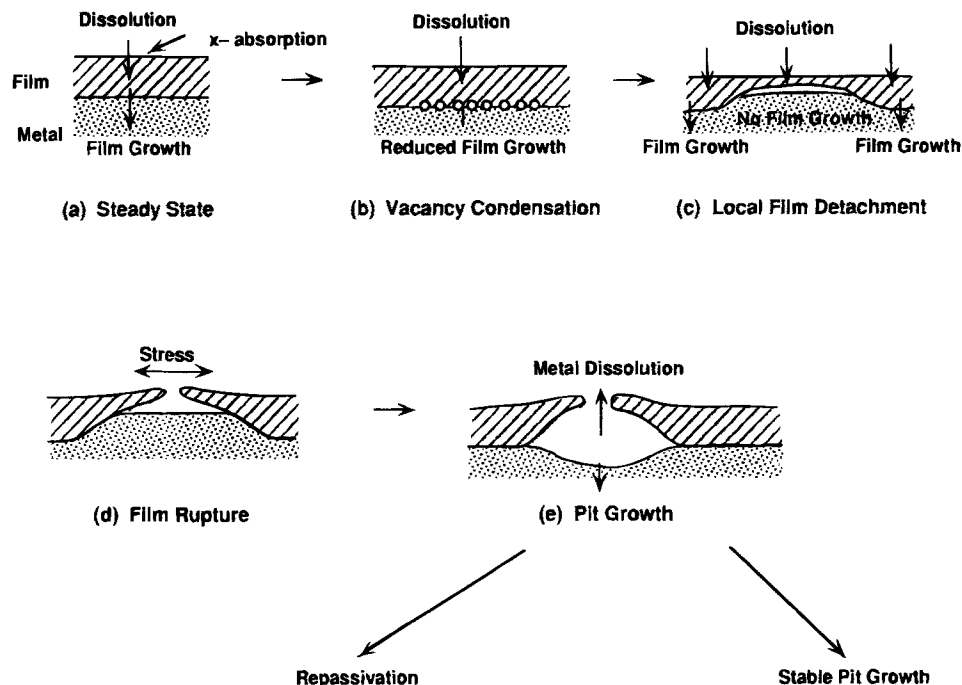


Fig. 2. Enhanced flux of cation vacancies through the passive film may occur on anion absorption at the barrier layer/environment interface (a), which eventually leads to localized detachment of the film at the metal/film interface (b). Detachment of the film retards film growth (c) compared to the rest of the film. However, film dissolution still occurs above the detachment. Film thinning continues until stresses in the film are sufficient to rupture the film and expose the bare metal substrate, (d). Growth of the blister is subsequently assisted by penetration of solution through fissures in the cap resulting in gas generation.

hence are not absorbed (as metal vacancies) into the metal substrate, they may condense, resulting in the local detachment of the film from the base metal. Clearly, these events will tend to occur preferentially at those points in the film where the cation vacancy diffusivity is highest (*i.e.*, at the so-called weak spots, such as at the boundaries between the barrier layer and precipitates, and at ghost grain boundaries). Once the film has become detached locally, growth of the barrier layer into the metal can no longer occur. However, dissolution of the detached film at the film/solution interface continues, thereby resulting in film thinning and eventual rupture, as depicted in Fig. 2. Thus, the cation vacancy condensation mechanism is characterized by the formation of blisters that eventually rupture to form pits.

If the cation vacancy diffusivity is low, as in amorphous films or films of high cation charge (*e.g.*, WO_3 on W), the vacancy pair created by ion desorption may persist at the film/solution interface. Case III of Fig. 1 illustrates this scenario, and we propose that the continued collection of vacancy pairs at the film/solution interface results in the destruction of the barrier layer at the film/solution interface.⁴ However, this mechanism does not appear to be viable as a direct cause of passivity breakdown, because destruction of the barrier layer at the film/solution interface should result in concomitant growth of the barrier layer into the metal substrate. It is possible that this eventually results in the formation of a local crevice, which may lead to passivity breakdown via an acidification mechanism. We term this mechanism indirect. Experimental evidence that the passive film on a solid substrate may undergo localized thinning is found in the work of Sugimoto *et al.*⁸ Using microscopic ellipsometry to study the passive film of 18Cr-8Ni stainless steel in chloride-containing solutions, they found a spatial distribution of film thickness within single grains, with pits nucleating at points where the film was thinnest. However, we hasten to add that localized thinning, alone, cannot be used to distinguish between cases I and II (cation vacancy condensation) and case III (vacancy pair coalescence), and one is still left with the difficulty in the latter case as to why the film simply does not thicken in response to the loss of mass at the film/solution interface by movement of the metal/film interface into the substrate metal.

Returning now to the first scenario, we suggest that cation vacancy condensates may increase to form macroscopic blisters by continued vacancy condensation at the

perimeter of the detached area. If so, and assuming that case I or II, Fig. 1, applies, one predicts that the absorption of the aggressive anion occurs most intensely at the periphery of the blister. These predictions are in accord with the observations of blisters by McCafferty *et al.*⁹ and Bargeron and Givens^{10,11} for the breakdown of passivity on aluminum in chloride-containing solutions. The latter researchers also report the blister to be surrounded by a chloride-containing ring. Also, Czachor *et al.*¹² have reported the formation of microstains on the surface of pure Fe that had been in contact with a chloride-containing solution, and these microstains are ring-shaped. These specimens were potentiostatically polarized below the pitting potential and no significant changes in the current density were detected. Additionally, closer inspection of a micrograph in this reference (Fig. 1a, Ref. 12) shows a faint ring around the microstain which we speculate to be a blister. Returning to aluminum, Bargeron and Givens^{10,11} also speculated that the solution penetrated through the disbonded oxide, resulting in the generation of hydrogen, which may provide a hydrostatic pressure that accelerates blister growth. Unbroken blisters on aluminum were found to evolve gases from a region approximately one radius width ahead of the advancing blister periphery.^{10,11} Further, Bargeron and Givens showed that the peripheries of the blisters are outlined by roughly circular rings of micropits which form as the blisters grow laterally in incremental steps along the inner interface of pure aluminum specimens. The PDM does not address events that occur subsequent to rupture of the blister, as has been previously emphasized.^{2,4} The most likely scenario is that proposed by Frankel *et al.*¹³ who suggest that rupture of the blister marks the nucleation of a metastable pit. If the exposed metal repassivates the metastable pit dies, but if conditions are such that the nucleus survives, stable pit growth results. Frankel *et al.* suggest that the critical factor in the transition of a nucleus from the metastable to the stable state is the precipitation of a salt film on the pit surface before the cover ruptures. However, it is not clear how the aqueous phase penetrates a truly intact film over a vacancy condensate. More likely, the intact cover that they refer to has fractured, and it is the resulting fissures that lead to the penetration of the environment and to the possible formation of a salt film.

Recently, Casillas *et al.*¹⁴ using scanning electrochemical microscopy (SEM), found that precursor sites for the nucleation of pits on the surface of Ti exhibited high electrochemical activity over a range of potential in the passive

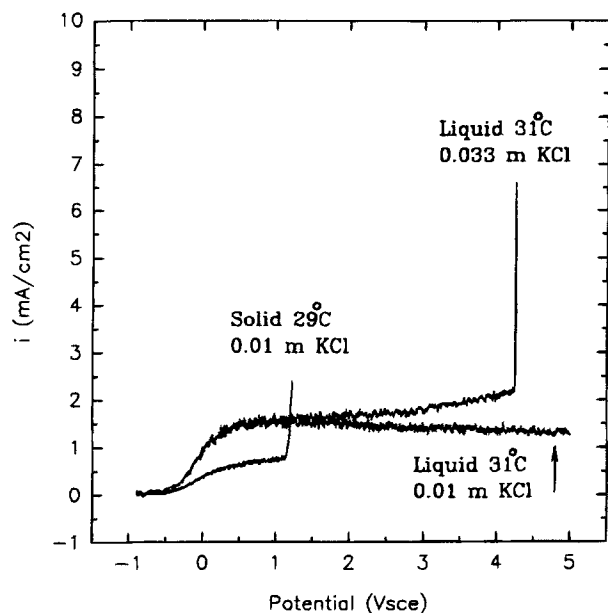


Fig. 3. Anodic polarization curves for solid and liquid Ga ($T_m = 29.78^\circ\text{C}$) in deaerated borate buffer 0.01 m KCl, showing the enhanced passivity of the liquid phase, and liquid Ga in deaerated borate buffer +0.033 m KCl. At the higher $[\text{Cl}^-]$, the film on the liquid phase does exhibit passivity breakdown. The potential scan rate was 0.5 mV/s.

region for this metal. Specifically, Br^- was oxidized to form Br_2 at these localized sites. This behavior may be explained⁷ by the localized absorption/desorption of Br^- and

subsequent generation of vacancies, in accord with the proposed mechanism for passivity breakdown (Fig. 1), and/or by the fact that the highly defective barrier layer at these sites is expected to have a high electronic conductivity and a high density of surface states, and hence to support a high local rate of electron transport. The experimental findings of Casillas *et al.*¹⁴ are shown elsewhere⁷ to be in excellent agreement with the predictions of the PDM, although this model was not employed by the original authors in interpreting their data. Finally, indirect evidence for vacancy condensation as the fundamental process leading to passivity breakdown on nickel,¹⁵ copper,¹⁶ and iron,² has been reported. The evidence is indirect, in the sense that support for the PDM is afforded by the excellent agreement between theory and experiment with respect to the dependence of the breakdown potential on chloride activity and the dependencies of the induction time on chloride activity and potential. In these cases, the barrier layers are so thin that any blisters formed are likely to be much smaller than can be resolved by optical microscopy and the induction time is dominated by vacancy condensation.

Passivity Breakdown on Gallium

Since a liquid conforms to its container, vacancy condensation does not occur readily and we predict that the passive film on a liquid metal resists localized breakdown more effectively than that on the solid substrate. This prediction is most readily tested using Ga, which exhibits a melting temperature of 29.78°C , and which is a passive metal not unlike aluminum. Surprisingly, little systematic work has been reported on the growth and breakdown of passive films on this metal, even though it can be obtained in a very pure state and exhibits advantageous properties for studies of this nature.

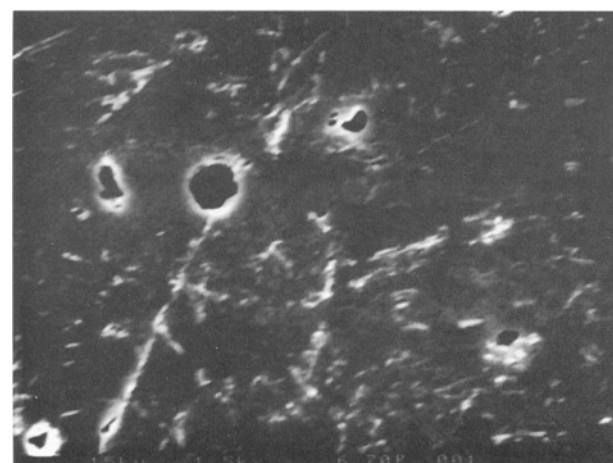
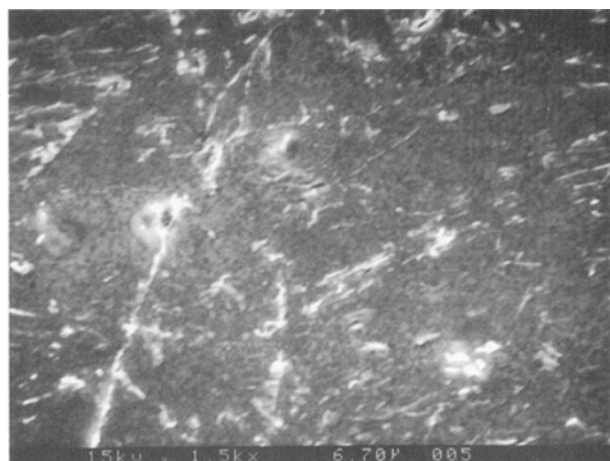
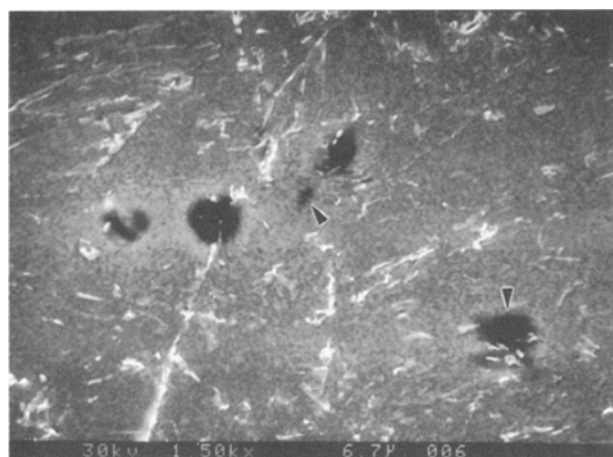


Fig. 4. SEM micrographs of a solid Ga electrode polarized in deaerated borate buffer +0.0033 m KCl. (a, top left) A high energy electron beam penetrates the film revealing blisters (center arrow) and detached film around a covered pit (lower right arrow); (b, above) a low electron beam does not penetrate the film; (c, left) ultrasonic cleaning removes the film and the pits become readily apparent at low beam voltages.

Anodic polarization curves for solid and liquid Ga in deaerated borate-buffer aqueous solutions containing 0.01M KCl, and that of liquid Ga in 0.033M KCl solution (pH 8), are shown in Fig. 3. In the low $[Cl^-]$ solution, solid Ga clearly shows a well-defined passive region and a transition into pitting attack, as indicated by the sharp rise in current. Evidence of blister formation and detachment of the film around the perimeter of a pit is given in Fig. 4 for a solid Ga specimen. The detached area (marked by the lower right arrow in Fig. 4a) is much larger than the pit observed (Fig. 4c) after ultrasonic removal of the film. These disbonded regions, only some of which were shown to cover geometrical pits (e.g., arrow in lower right corner, Fig. 4a), were detected by using a high voltage electron beam (25 to 30 kV) to penetrate the film during SEM examination, and by subsequent ultrasonic cleaning of the specimen to remove the film. An example of a detached area that was found not to cover a geometrical pit that could be resolved by SEM is indicated by the arrow in the center of Fig. 4a. Barger and Givens,¹⁰ also used this SEM technique, in combination with *in situ* microscopic observation of blister formation. Hence, the blisters did not result from the vacuum applied to the specimen during SEM analysis, but formed *in situ* during exposure to the solution.

As also shown in Fig. 3, liquid gallium (at 31°C) exhibits a passive region extending to 5 V_{SCE} in 0.01M KCl solution. Because the initial passive film on the liquid electrode was formed on the solid substrate (since the solid was melted *in situ*), and presumably contains the same impurities and structural defects, the lack of breakdown on the liquid substrate, in this case, argues strongly against the properties of the passive film as being the controlling factor. Rather, we propose that our observation is consistent with the PDM in that vacancy condensates do not readily form at the metal/film interface on a liquid substrate. A similar result is obtained if the Ga is maintained in the liquid state throughout the entire experiment, so that the transition from the solid phase to the liquid phase in the experiment described above cannot account for the difference in polarization behavior between the solid and the liquid substrate shown in Fig. 3. Finally, at a sufficiently high chloride concentration (Fig. 3), passivity breakdown can be induced on liquid Ga, but the form of attack is different from that observed on the solid, being in the form of dissolution over large but discontinuous areas of surface and subsequent formation of visible precipitates, rather than in the form of highly localized attack, as discussed below. The experiments described above have been repeated many times and are reproducible.

During optical microscopy of liquid specimens that had been polarized anodically in deaerated borate buffer +0.001M KCl solutions, the intact passive layer may be seen and passivity breakdown was found not to have occurred. The surface is free of dark oxide precipitates and it is the same in appearance as wrinkled aluminum foil. An increase in chloride concentration to 0.01M KCl causes narrow, stringlike precipitates to form; however, these specimens were anodically polarized to 5 V_{SCE} and still did not suffer passivity breakdown, as indicated by the absence of a sharp rise in the current. Apparently, a localized precipitate layer forms above the passive film due to enhanced (chloride-catalyzed) cation transmission, while still maintaining the barrier layer intact. This behavior is expected because of the ever increasing voltage that exists across the film by the imposed potential sweep. However, polarization in a solution of sufficiently high chloride activity does result in passivity breakdown on liquid Ga as indicated by the current response shown in Fig. 3 for 0.033 M KCl. At still higher $[Cl^-]$, the surface of the film on the liquid substrate is partly covered by a dark precipitate, and holes (Fig. 5) and depressions in the film (as detected using a scanning laser microscope) suggest that the precipitates form by localized general attack that is different from that which occurs on the solid.

During the review of this paper, two of the three referees suggested that our findings could be interpreted on the ba-

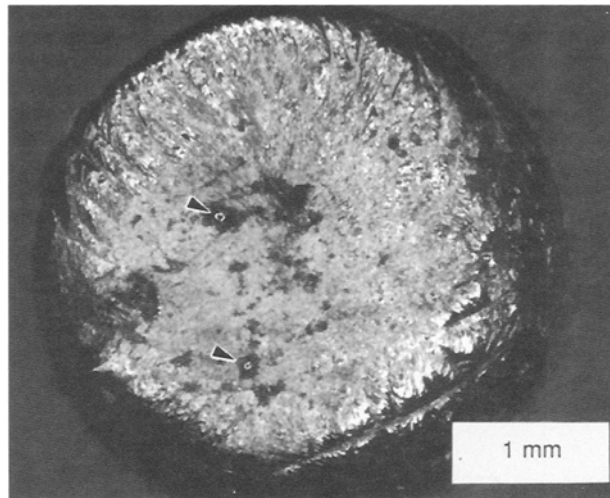


Fig. 5. Optical macrograph of liquid specimen polarized in deaerated borate buffer +0.1 M KCl solution, showing two holes in the film.

sis that liquid Ga cannot form a geometrical pit, and that the lack of a rise in the current at high voltages (but at low chloride activity) is simply a manifestation of the fact that aggressive conditions cannot develop at the breakdown site. However, as shown in Fig. 3, passivity breakdown does occur on liquid Ga, and the current does rise, if the specimen is polarized to sufficiently positive voltages in a solution of sufficiently high chloride activity. Thus, the formation of a geometric pit is not a necessary or sufficient condition for the sudden increase in the current and we reject this argument as providing a viable explanation of the data. Clearly, as indicated by the data for liquid Ga, passivity breakdown is a sufficient condition for the current rise and is a precursor to pit formation. One referee also argued that the lack of a sudden increase in the current on liquid Ga, on polarizing the specimen in the positive direction, is due to rapid repassivation of the breakdown sites, such that an increase in current is not observed. However, assuming that repassivation is an anodic (oxide formation) process, one expects repassivation to become more rapid with increasing potential, and hence one predicts that the current should never rise. As is evident from Fig. 3, the current does rise on the liquid substrate, provided that the voltage and chloride activity are sufficiently high. Further, passivity breakdown in a precursor event to repassivation. Thus, we also reject this mechanism as providing a viable explanation of our experimental data.

In closing, we note that numerous examples of blister or void formation, and ruptured pits have been observed beneath the passive films on aluminum,¹⁷ stainless steels,^{13,18,19} zirconium,²⁰ and now gallium, under conditions where passivity breakdown occurs. In some cases (e.g., Al) it has been demonstrated that the blisters are precursors to the initiation of pitting corrosion. Further, the inhibition of passivity breakdown on a liquid metal substrate, compared with a solid, is readily accounted for by the PDM, by noting that vacancy condensates do not readily form beneath the passive film on a liquid substrate. While other models of passivity breakdown may explain the observations reported here, specific mechanisms have yet to be proposed.

Acknowledgment

The authors thank the U.S. Department of Energy for the support of this work through Grant No. DE-DG03-84ER45164.

Manuscript submitted Dec. 6, 1994; revised manuscript received May 19, 1994.

The Pennsylvania State University assisted in meeting the publication costs of this article.

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Fluorine-Passivated Electroless Ni-P Films

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ABSTRACT

An optimal nickel difluoride (NiF₂) film-formation technology has been investigated for electroless Ni-P deposited films, where highly sensitive electrochemical anodic polarization measurement and thin-film x-ray diffraction (XRD) studies using low incident angle have been employed to establish this technology. Electroless Ni-P deposited films have an amorphous structure as deposited which is converted into crystalline structure such as nickel phosphides (Ni₂P or Ni₃P) with heating, this is undesirable for the formation of homogeneous fluorine passivation films. Low incident angle XRD allows us to determine the fluoridation conditions where the NiF₂ films little include these nickel phosphides crystals. Further, anodic polarization measurement curves support the film-formation conditions (temperatures, fluorine concentration) of nickel difluoride and the effect of heat-treatment after fluoridation. The low fluoridation temperature at ca. 300°C is not sufficient and low fluorine concentration is also unfavorable for the fluoridation of the electroless Ni-P deposited films. We conducted several evaluations such as corrosion resistance, outgassing characteristics, and plasma resistance using the nickel difluoride films formed by the most favorable condition.

Accurately controlled semiconductor manufacture processing is essential for the effective improvement of reproducibility and yields as semiconductor devices become more highly integrated. This demand becomes increasingly indispensable for device processing in the near future.^{1,2} Slight fluctuations in process conditions cannot be permitted for the achievement of these goals. We believe process conditions should be maintained always at the initial condition based on the design. Presently, several reactive and corrosive speciality gases are used in semiconductor fabrication. Hence, several fluctuations are caused during processing and from wafer to wafer for such reasons as quantitative variations due to metal corrosion and catalytic decomposition of gases themselves.³ This result in the metal or decomposition product contaminating the wafer surfaces. To overcome these problems, we have examined the passivation technology reported previously in more detail.⁴ In the previous report, we investigated the fluoridation mechanism of the electroless Ni-P deposited films and

found that the NiF₂ film formed contains no phosphorus in it and is thicker than that formed by fluoridation of pure Ni. As many workers have reported, however, the electroless Ni-P deposit films have an amorphous structure as deposited, which converts to crystalline structure upon heating, that is, formation of nickel phosphides (Ni₂P, Ni₃P). Lin and Lai have reported that heat-treatment at temperatures above 300°C gives rise to Ni and Ni₃P phases.⁵ Allen and VanderSande have shown that the crystallization of face-centered cubic (fcc) Ni in an amorphous Ni-P matrix takes place at 247°C, while the precipitation and growth of Ni₃P occurs above 367°C.⁶ In addition to the above, the existence of these nickel phosphides have been shown for electrodeposited Ni-P films by Masui *et al.*⁷ These nickel phosphides are metastable or stable structures which do not react easily with fluorine under mild fluoridation conditions. It is important not to form these nickel phosphides during fluoridation for achievement of the passivation technology. An attempt has been made to form homogeneous nickel difluoride films.

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